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# BioProgrammable One-, Two-, and Three-Dimensional Materials

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14. ABSTRACT
The MURI team has used biomolecules (such as DNA or peptides) to assemble nanoparticles into highly ordered one-, two-, or three-dimensional architectures. The Mirkin group has used DNA-functionalized nanoparticles as "programmable atom equivalents (PAEs)" as material synthons to synthesize hundreds of different crystal structures. The Macfarlane group developed methods to combine bottom-up DNA directed assembly with electron beam lithography to simultaneously control material structure at the nano- and macroscopic length scales. The Nguyen group has synthesized and assembled small molecule-DNA hybrids (SMDHs) as part of programmable atom equivalents. The Rosi group identified design rules for using peptide constructs to direct rational assembly of inorganic nanoparticles into ordered hierarchical nanoparticle superstructures, including hollow spherical structures and 1-D helical nanoparticle arrays exhibiting strong plasmonic chiroptical response. Theoretical studies as well as various characterization techniques were studied in conjunction with all of the abovementioned experimental approaches to construct new materials with biomolecule-functionalized building blocks. The Schatz group developed electrodynamics models of plasmonic superlattices to identify unique optical behavior of these materials, including negative permittivity, Fabry-Perot resonances, and nonreciprocal properties. The Olvera group predicted the shape of single crystals of DNA-functionalized nanoparticles and their nucleation behavior. The Bedzyk group utilized in-situ X-ray scattering and spectroscopy to develop fundamental understanding of PAE constructs, from their synthesis and electrostatic environment, to inter-PAE interactions that affect programmable assembly. As a whole, the MURI team synthesized, measured, and evaluated a set of new materials with specific properties by design.

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## ABSTRACT

Under this MURI, the Mirkin group along with others assembled nanoparticles into well-defined and controllable geometries utilizing rigid organic biomolecules. Upon formation, such particles are functionalized with synthetic oligonucleotides, and the entire construct is incorporated into assembly systems as a single type of building block for forming higher-ordered nanoparticle architectures. Design rules were established *a priori* and nanoparticle superlattices can now be programmably assembled in a variety of sizes, symmetries, and shapes with DNA. One can now assemble superlattices with material compositions beyond gold (e.g. quantum dots, iron oxide, and platinum particles), or build them in a layer-by-layer fashion on planar substrates. Anisotropic nanoparticles can be used to template unique low-dimensional superlattice symmetries that exhibit novel properties. The Mirkin group has also investigated different methods to control superlattices post-assembly to access dynamic structures. The Macfarlane group has established methods to use lithographic templates to control the epitaxial deposition of DNA-linked nanoparticle superlattices, thereby generating single crystalline nanoparticle-based materials over mm-sized areas. Furthermore, the Macfarlane group has also established a new class of composite building block that utilizes supramolecular chemistry to control inorganic particle positions within an organic polymer matrix. The Nguyen group has designed and synthesized SMDHs with well-defined numbers and spatial geometries of oligonucleotides as molecular PAEs, assembled pure organic-cored supramolecular structures, and studied their DNA hybridization behavior, both experimentally and theoretically. Peptide-based methods were developed by Rosi and others for rationally controlling the assembly of inorganic nanoparticles into hierarchical nanoparticle superstructures. Peptide conjugate molecules of the general constitution $C_x$-$(PEP_{In})_y$ were used to direct the assembly of particles and were systematically modified to control and design the morphology of the nanoparticle superstructure. The Schatz group used theory and computation to study and predict the structural and optical properties of DNA-linked nanoparticle superlattices and of peptide amphiphile nanoparticle aggregates, providing interpretation and prediction for both synthesis and characterization work in the MURI. This led to the elucidation of rules for the self-assembly for superlattices and peptide amphiphile micelles, and many unusual superlattice optical properties. The Olvera group extended the flanking bead model to a coarse-grained model that studies DNA chains that are bonded to a rigid core. Using this extended model, the Olvera group recovered experimental phase diagrams obtained from binary mixtures of DNA-coated spherical gold nanoparticles. The Bedzyk group has developed and utilized X-ray methods to reveal subtle features of PAE constructs and interactions that are not discernible by other methods. From a bottom-up approach, X-ray spectroscopy and scattering were used to probe the structure of the nanoparticle core, oligonucleotide shell, counterion-cloud and inter-PAE electrolyte-mediated interactions.

## OBJECTIVES

The specific goals are as follows:

1. Establish a set of design rules for using biomolecules (oligonucleotides and peptides) to assemble nanoparticles into highly ordered one-, two-, and three-dimensional structures.
2. Develop a methodology to incorporate "bottom-up" directed assembly techniques with "top-down" soft-matter compatible lithographic techniques to enable the synthesis of ordered two- and three-dimensional constructs that can interface with macroscale devices.
3. Develop theoretical models to predict assembly parameters and to understand the physical properties that arise from assembled structures a priori.
4. Experimentally measure and evaluate the novel emergent physical properties of these systems, and to develop a library of information to enable future materials development. Indeed, the work should lead to the ability to make fundamentally new materials with specific properties by design. When a technological device is used or targeted in the proposed work, the goal is to extract fundamental information about a given system as opposed to the development of a particular technology.

## FINDINGS

To date, research on bioprogrammable materials in one-, two-, and three-dimensions has resulted in many publications in high-impact journals (i.e., *Nature, Nano Letters, PNAS, Angewandte Chemie, Nature Materials, Science, JACS, Nature Nanotechnology, and Advanced Materials*). Most of these publications entail the assembly of nanoparticles into well-defined and controllable geometries utilizing rigid organic molecules. Upon formation,

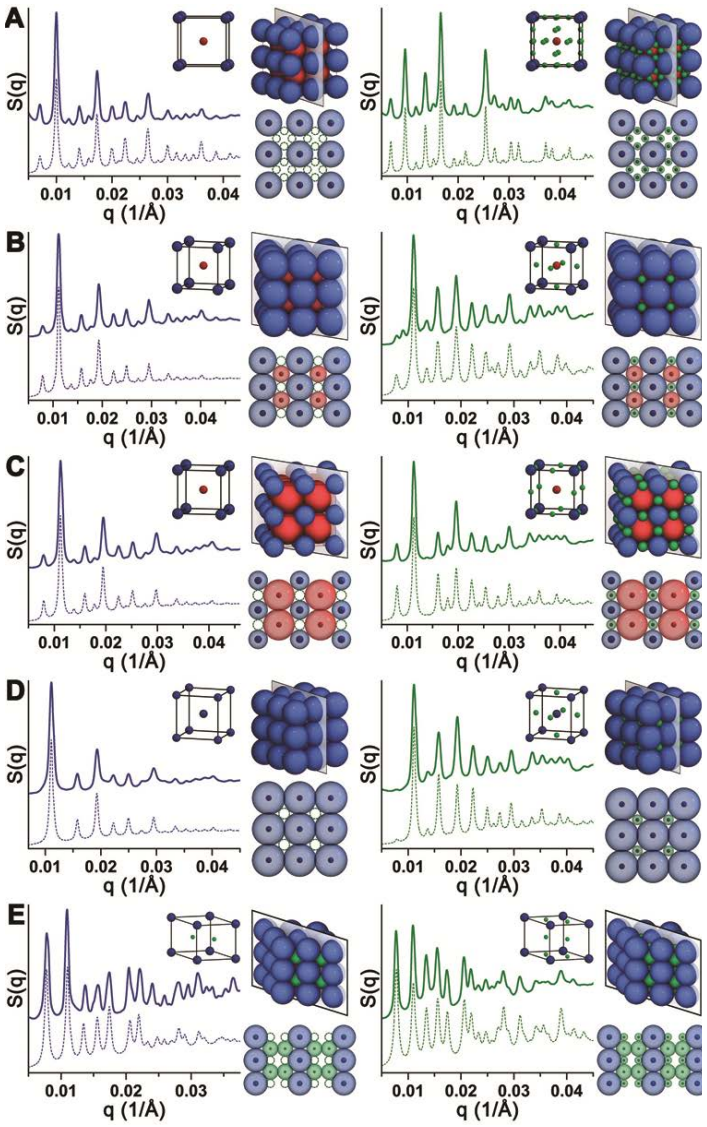


**Figure 1. Schematic illustrations and small angle X-ray scattering spectra of the five new nanoparticle superlattices formed through topotactic intercalation. "Parent" superlattices are shown on the left and "daughter" superlattices on the right. Assemblies are isostructural with (A) CsCl and $ABC_{12}$-type, (B) CsCl and face-perovskite, (C) CsCl and edge-perovskite, (D) bcc and $A_2B_3$-type, and (E) $AlB_2$- and $AB_4$-type geometries.**

the nanoparticles are functionalized with synthetic oligonucleotides, and the entire construct is incorporated into assembly systems as a single type of building block for forming nanoparticle superlattices.

**Mirkin** and all MURI collaborators have demonstrated how DNA can be used to synthesize a wide variety of lattices with independent control over nanoparticle size, crystal symmetry, and lattice parameters, by controlling the length and nucleobase sequence of DNA linkers used to direct nanoparticle superlattice formation (see Figure 1). Further, **Mirkin** and collaborators have developed a set of design rules that explain the stability of different lattices and allow for *a priori* determination of the DNA designs necessary to synthesize a desired lattice. However, all of the lattices synthesized to date utilize at most two unique nanoparticle components, and post-synthetic modification was limited to thermally induced changes to lattice parameters.

In 2012, **Mirkin** demonstrated using hollow "spacer" particles, where the core nanoparticle composition plays no role in the assembly process, making this DNA-based strategy for superlattice assembly a truly materials general technique. However, the main limitation in extending this early work to construct lattices with nanoparticles composed of materials besides noble metals is the development of a DNA functionalization strategy. The thiol chemistry used to attach DNA to gold and silver is not applicable to other nanoparticles that may be of interest, such as cadmium selenide, iron oxide, or palladium, which exhibit unique photonic, magnetic, and catalytic properties, respectively.

In 2013, **Mirkin** successfully met this challenge by developing a polymer-based coating technique to load a dense layer of DNA strands onto nanoparticles of arbitrary composition. This technique involves taking nanoparticles functionalized with hydrophobic small molecules (for which multiple syntheses have already been established), and coating them in an amphiphilic polymer containing multiple azide moieties. These azide moieties can then be reacted with alkyne-bearing DNA strands via the copper-free Huisgen cycloaddition "click" reaction, resulting in nanoparticles coated with a dense monolayer of oligonucleotides. To date, this technique has been successfully applied to quantum dot (CdSe/ZnS), iron oxide ($Fe_3O_4$), gold, and palladium nanoparticles. A series of studies have confirmed that these newly achieved DNA functionalized nanoparticles have similar properties as the thiolated DNA modified AuNPs, such as high density of DNA loading on each particle, cooperative binding with complementary nucleic acids, etc. Most importantly, the as-synthesized DNA-functionalized nanoparticles behave the same as thiolated DNA-AuNPs in superlattice self-assembly, enabling the fabrication of DNA directed 3D crystal structures of a vast array of PAEs where one can control particle size, shape, and composition, as well as lattice parameters and crystal symmetry of an assembled structure.

Over the years, experimental observations on superlattices synthesized using the DNA-programmed approach have shown that the resulting material is polycrystalline, comprised of randomly-oriented micron-sized grains, and do not exhibit facets typically observed in common atomic crystals such as table salt. In 2014, **Mirkin** has demonstrated a slow-cooling crystallization method for controlling the growth of DNA-assembled nanoparticle superlattices into rhombic dodecahedron single crystals with well-defined facets (Figure 2). An understanding of the observed single crystal growth was elucidated through a combined approach using experiment, theory, and simulation by **Olvera de la Cruz**. This work has shown that the growth of nanoparticle single crystals, although assembled through DNA base-pairing rather than atomic interactions, is consistent with the growth pathways and kinetics observed by atoms during their crystallization into higher order structures. Experiment and simulations confirm that the observed crystal shape, the rhombic dodecahedron, forms from a bcc superlattice because this shape minimizes the overall

surface energy by exposing the lowest energy (110) facet. Future work will focus on designing and predicting additional microcrystal shapes through surface energy minimization.

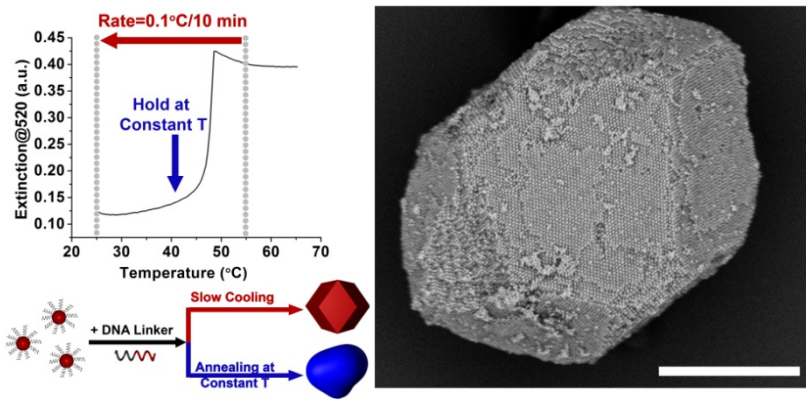


**Figure 2. Slow cooling crystallization allows for single crystal formation from DNA-nanoparticle superlattices where traditional annealing has only resulted in polycrystalline domains. Scale bar 2µm.**

For a few years, **Mirkin** work on the assembly of PAEs was focused on the crystallization behavior of PAEs with spherical nanoparticle cores. Additional complexity and structural control can be introduced with PAEs containing anisotropic nanoparticle cores. Anisotropic PAEs crystallize with directional DNA bonding interactions perpendicular to each nanoparticle face. Face-to-face interactions emerge in these systems due to the increased number of DNA hybridization events that can occur between the flat surfaces of oriented anisotropic particles.

**Mirkin** utilized the sequence programmability of surface-bound DNA ligands to force the cocrystallization of a range of different anisotropic nanoparticles and systematically investigated how structural complementarity impacts the formation of crystalline materials. This work was enabled by recent MURI-supported efforts by **Mirkin** for the synthesis of highly uniform anisotropic nanoparticles with tunable sizes and shapes (Figure 3). In this work, **Mirkin** split structural complementarity into two categories: size complementarity and shape complementarity. The size complementarity was defined as the dimensional similarity between the interacting facets of two nanoparticles (Figure 3c), and shape complementarity as how efficiently the interacting facets of two nanoparticles pack together in three-dimensional space, analogous to a lock and key concept (Figure 3d). To investigate shape complementarity in DNA-mediated cocrystallization, cubic

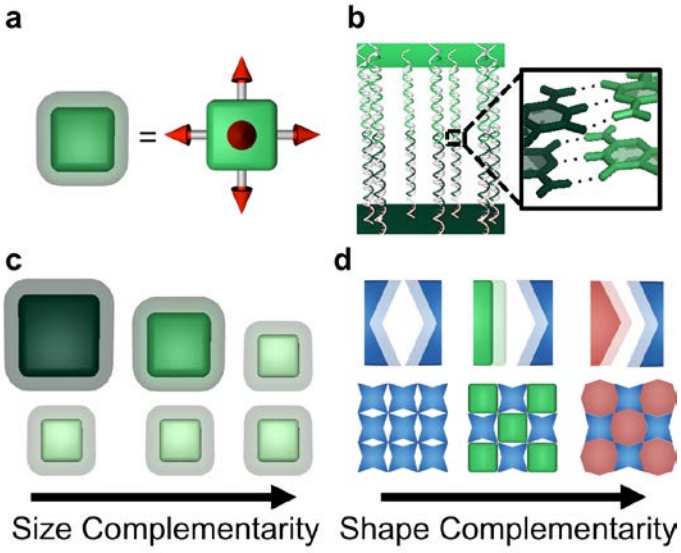


**Figure 3. a) Nanoparticle shape can be used to template the arrangement of surface-bound DNA ligands. The resultant shell of DNA (light green) interacts with other nanoparticles in a directional fashion (red arrows). b) Many complementary DNA hybridization events between two interacting nanoparticles mediate crystallization. c) Size complementarity between two nanoparticles is controlled by the differences in the characteristic dimension of the nanoparticles. d) Shape complementarity between two nanoparticles is controlled by the alignment of directional interactions in three-dimensional space.**

nanoparticles of the same size, but different degrees of concavity or convexity were assembled (Figure 3). This approach allows one to maintain a consistent cross-sectional shape and interaction area between two nanoparticles, while systematically changing the degree of shape complementarity. Specifically, **Mirkin** and collaborators investigated 1:1 mixtures of concave cubes, cubes, and convex cubes with L = 65 nm, where the maximum depth of the concave or convex features was ~10 nm (Figure 3). Each of these nanoparticle shapes should template a unique arrangement of DNA ligands, as the DNA shell has been shown to conform to the underlying shape of the nanoparticle (Figure 3). Because particle association is driven by the precise alignment of a complementary 5-base region at the terminus of each DNA strand, one would expect the concave or convex nanoparticle features to significantly impact the ability of particles to form DNA connections uniformly across the particle-particle interface. Therefore, it was hypothesized that greater shape complementarity would result in a greater overlap between the DNA shells of adjacent nanoparticles, resulting in a greater number of DNA connections to guide cocrystallization. This, in turn, should manifest in a greater degree of long-range order and potentially in the formation of single crystalline superlattices.

Collectively, these results establish a systematic understanding of how the structural complementarity of two anisotropic nanoparticle-based PAEs impacts crystalline structure. Furthermore, this work significantly advances the ability to predict both the likelihood of forming a well-ordered crystal and a well-defined macroscopic crystal structure (*e.g.* habit, size, defect structure) based on the identity of the building blocks. Such control should inform theoretical work aimed at elucidating target structures for the exploration of emergent optical properties.

**Mirkin** has demonstrated that lattice complexity can be increased substantially through a method of topotactic intercalation—the process of inserting additional nanoparticle components into a preformed superlattice structure. This was achieved by synthesizing "parent" DNA-NPs that could form relatively strong DNA linkages with one another, and "daughter" DNA-NPs that could only weakly bind to the parent particles. This allowed us to define a temperature regime wherein the "parent to parent" linkages were stable, but the "parent to daughter" linkages were not, enabling the synthesis of lattices in a two stage process (Figure 4). The parent particles were first assembled into a lattice at high temperature; once

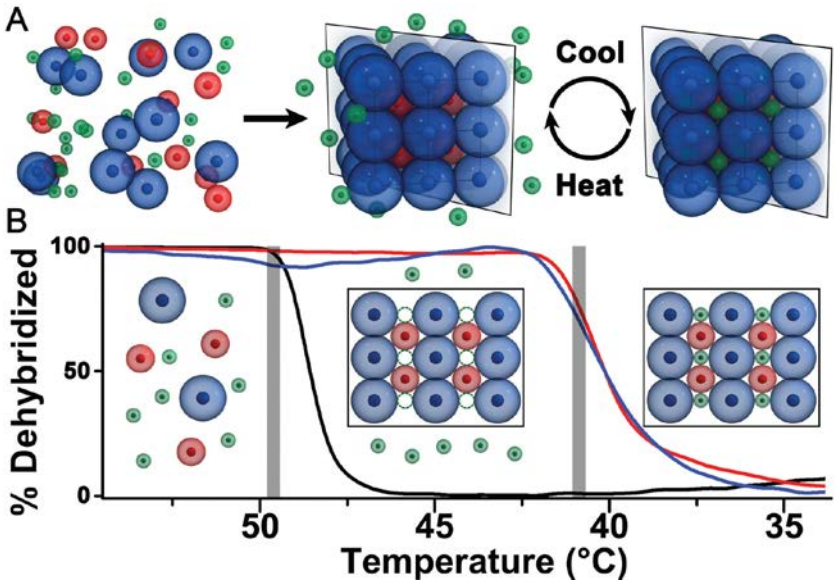


**Figure 4. Conceptual illustration of the topotactic intercalation of "daughter" NPs (green spheres) into a "parent" superlattice (blue and red spheres) by designing the respective DNA interactions to occur at significantly different temperatures.**

formed, the daughter particles were then added to this lattice, whereby they intercalated into the parent structure, forming a new lattice symmetry.

In addition to demonstrating the topotactic intercalation of nanoparticles into preformed superlattices, **Mirkin** has shown that dynamic control of superlattices can also be accomplished using oligonucleotide effectors to expand and contract the lattice *in situ*. When superlattices are assembled with DNA hairpin structures incorporated into linker strands, oligonucleotide effectors can be added to "open" or "close" the hairpin structures. This change in the overall length of the nanoparticle-immobilized DNA increases or decreases the interparticle distance and therefore dynamically expands or contracts the entire lattice (Figure 5). The superlattices can be driven to the opened and closed states through multiple cycles in such a way that the crystal symmetry and overall crystal quality is maintained while toggling between states. This process can be implemented to a variety of crystalline lattice structures including FCC, BCC, CsCl, etc., demonstrating the versatility of the hairpin duplex design.

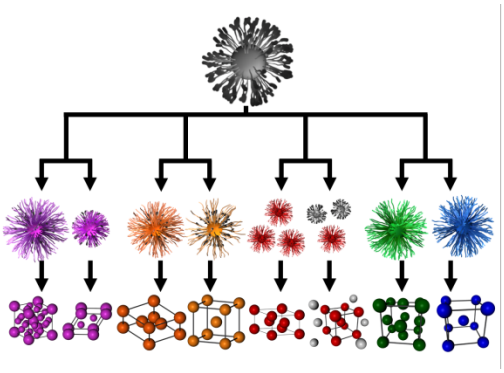

**Figure 5. Schematic of different crystallization pathways of a "transmutable nanoparticle"**

Specifically, we showed that DNA-based hairpin ligands, which undergo well-defined conformational changes upon binding of effector oligonucleotides, can be used to alter the bonding properties of the nanoparticles. Inspired by pluripotent stem cells, which are capable of differentiating into multiple biological tissues, we introduced the concept of a transmutable nanoparticle, a materials building block with different possible binding characteristics that can be selectively activated and deactivated with the appropriate chemical cues and then used to generate discrete forms of complex crystalline matter.

The primary goal of the optical property modeling work was to understand and predict the interaction of light with superlattice materials that contain silver and gold nanoparticles.

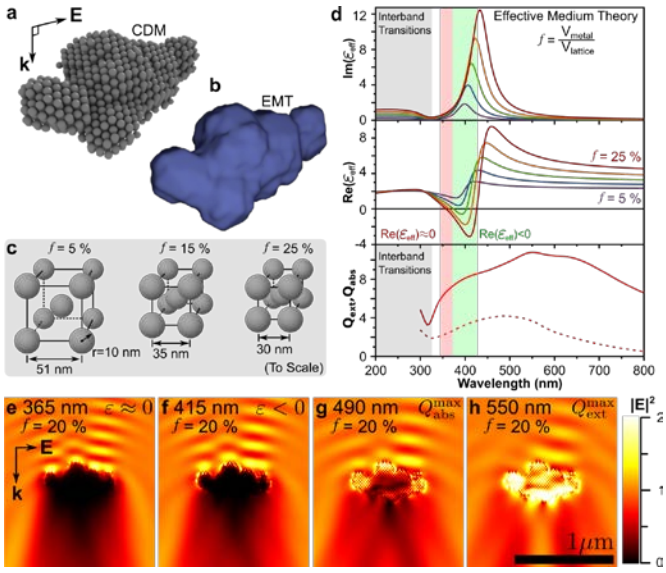


**Figure 6. a) Randomly generated superlattice of Ag NPs, chosen to match the experiments. b) Scheme showing the structure as simulated in Effective Medium Theory (EMT): the internal detail of the superlattice is replaced with a continuous material with a dielectric function described by Maxwell Garnett EMT. c) The relationship between particle radius and lattice constant, showing the proximity of the nanospheres in the lattice. d) Optical constants of an Ag NP superlattice with fill fraction, *f*, varying between 5% and 25%. e) Incident electromagnetic field at 365 nm, demonstrating Epsilon-Near-Zero (ENZ) material behavior. f) Incident electromagnetic fields at 415 nm showing metallic behavior. g) Incident electromagnetic field at the absorption maximum, 490 nm. h) Incident electromagnetic field at the extinction maximum, 550 nm.**

This was primarily a collaboration of **Schatz** and **Mirkin,**[1-4] but there were also connections of **Schatz** with nanoparticle helix work involving **Rosi**.[5-6] A key component of the **Mirkin** collaboration was to develop and validate the use of effective medium approximations for modeling the extinction spectra of superlattices, as this simplification enabled the use of simple analytical models that could easily be used to predict results for a wide range of structures. An important results from the MURI was the discovery that the effective medium permittivity of superlattices involving silver particles (but not gold) can be negative at wavelengths close to 400 nm (Figure 6).[4] The figure demonstrates that at metallic frequencies there is little light penetration into the superlattice structure (i.e., the material reflects), while at other wavelengths where the permittivity is positive, there is strong transmission and electromagnetic hot spots. This unique behavior of silver superlattices stimulated additional theory and experimental projects. One example involved the use of films of mixed silver/gold superlattices with composition gradients to observe asymmetric reflectivity (where the reflectivity is different depending on whether the light is incident on the silver on the gold-rich or silver-rich sides).[1] Very recently this concept has been generalized to the transverse magneto-optic Kerr effect (TMOKE), where theory calculations have been used to demonstrate nonreciprocal reflection associated with a layer of superlattice material combined with a layer of cobalt.[7] Figure 7 shows an example of the results, here showing that the sign of the TMOKE parameter δ associated with reversing the magnetic field direction, i.e., $\delta = \frac{R(+M) - R(-M)}{R(+M) + R(-M)}$ where R(+M) is the reflectivity for field M, changes from negative (its value for cobalt without the film, or for an Au SL) to positive over the range of wavelengths near 400 nm where the Ag SL has negative permittivity.

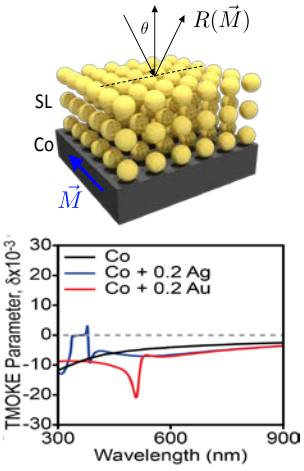


**Figure 7. Top: Geometry of the TMOKE measurement. Bottom: TMOKE parameter δ as function of wavelength for a Co film, a Ag SL film on Co, and a Au Sl film on Co. The superlattice films have volume fractions of 0.2.**

An additional direction of the Schatz work has been shown that superlattice growth can be directed into mesoscopic shapes analogous to Wulff shapes with well-defined crystal habits. Using the coupled dipole method, effective medium theory, and anomalous diffraction theory (a geometric optics approximation), rod-shaped superlattices are shown to confine and scatter light to the far-field similar to optical fibers.[3] This unusual light scattering is explained by an elevated refractive index far from the typical metal nanoparticle optical signature; it is the result of their close proximity and increased volume fraction. Current experimental work is underway to probe the effect of particle spacing and superlattice size on superlattice scattering and light confinement.

In another experimental-theoretical study by **Schatz** and **Mirkin** it was shown that mesoscopic single crystal superlattices with well defined crystal habits have inherently different optical properties when compared to thin film superlattices, even when they are comprised of identical nanoparticle crystalline arrangements.[3] That is, mesoscale crystal habit can be used to influence the optical properties of plasmonic superlattices. Also demonstrated is that the optical response of the crystal habit (due to photonic scattering) can be fine-tuned by changing the spacing between constituent nanoparticles. Ultimately, this means that the optical properties of a superlattice can be rationally designed to be either plasmonic (dominated by the nanoparticles) or photonic (dominated by the crystal habit) by changing the nanoparticle spacing or symmetry. As an

extension of this work, five different crystal habit superlattices (cube, rhombic dodecahedron, sphere, cylindrical disk, triangular prism) were used to study the effect of crystal shape on the optical response. Each shape is found to have distinct optical properties, suggesting that future advances in controlling crystal habit in plasmonic superlattice systems will enable the deliberate and precise control over the optical response.

In related work, **Schatz** and **Mirkin** have explored the role of crystalline defects and inhomogeneity in DNA-nanoparticle superlattices and the effect that they have on the optical response. In this work it was identified that many of the optical properties identified to date in nanoparticle superlattices are robust to nanoparticle polydispersity and to nanoparticle misplacement in the amounts that are typically present experimentally. At higher volume fractions, ~20-25%, it was identified that the properties of the superlattices are not accurately described by volume fraction, and specific nanoparticle models must be used to predict and understand their optical response.

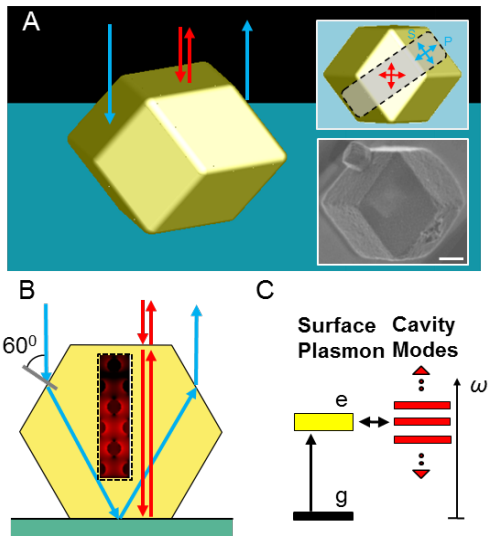


**Figure 8. A PPC made by DNA-programmable assembly. (A) 3D illustration of a plasmonic PPC assembled from DNA-modified gold nanoparticles. Red arrows indicate light rays normal to the underlying substrate (FPMs). The blue ones represent light rays entering through the slanted side facets. The top right inset shows a top view of the crystal. The bottom right inset shows an SEM image of a representative single crystal. (Scale bar, 1 μm.) (B) A 2D scheme showing the geometric optics approximation to backscattering consistent with the explanation in A. The hexagon outline is a vertical cross-section through the gray area in the top right inset of A parallel to its long edge. The box enclosed by a dashed line depicts the interaction between localized surface plasmons and photonic modes (red arrows; FPMs) with a typical near-field profile around gold nanoparticles. (C) Scheme of plasmon polariton formation. The localized surface plasmons (yellow bar) strongly couple to the photonic modes (red bars; FPMs).**

Recent theoretical work by **Schatz** and **Mirkin** has suggested that photonic crystals consisting of metal nanoparticles can induce a photonic band gap that involves strong coupling between surface plasmons and photonic modes when the lattice constant of the superlattice crystals is in the deep subwavelength size regime. Such crystals have been labeled polariton photonic crystals (PPCs). The work by **Mirkin** and **Schatz** demonstrated the fabrication and optical capability of PPCs as the first device application based on the DNA assembly technique. The PPCs exhibit Fabry–Perot cavity modes (FPMs) due to two parallel facets in the microcavity geometry (Figure 8a) and the FPMs can be detected via backscattering spectra. The optical response of the PPCs can be analyzed by the spectra, and the results demonstrate that light can strongly couple to the gold nanoparticle surface plasmons in the PPCs (Figure 8c), forming a polariton band gap at the surface plasmon frequency. Good agreement is demonstrated between the measured and predicted Fabry-Perot optical properties

Overall these optical studies have demonstrated that DNA programmable colloidal crystallization can be used to create plasmonic PPCs with finely tailored lattice constants and nanoparticle diameters. The observed control over light-matter interaction is unprecedented in the studies of based on metal nanoparticle crystals.

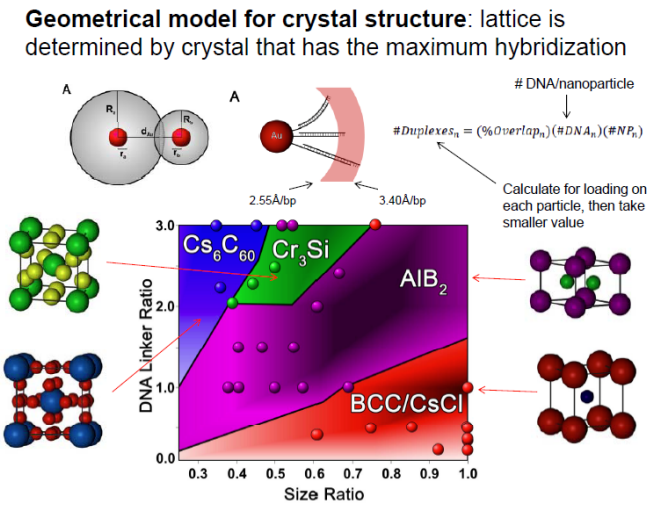


**Figure 9. Model of superlattice structures for DNA-linked gold nanoparticles.**

In the first year of the grant, a simple geometrical model of DNA-linked superlattice structures with spherical gold particles with two different sizes, or two different DNA-loadings was developed in collaboration between **Schatz** and **Mirkin**.[8] Figure 9 shows the predictions of the model, as well comparisons with experiment. This work provided the basis for a significant component of the synthetic work during the remainder of the project. In addition, this stimulated a collaboration of **Schatz** and **Olvera** in which coarse-grained molecular dynamics methods were developed to determine superlattice structures that are associated with gold triangular prisms. Thus the coarse-grained approach provides a powerful tool for studying the structures of DNA-linked nanostructures in which particles of arbitrary shape and size are co-crystalized. However, all-atom models are also important for understanding some properties of these systems. An important example of this was concerned with whether the DNA which links gold particles together can be A-form, as A-form DNA is normally not stable under the aqueous conditions and salt concentrations that are used in the synthesis. These molecular dynamics calculations which start with either A to B form DNA placed between two gold particles with the interparticle distance chosen to match experiment. The simulations show that B-DNA is bent when the interparticle distance is constrained to have its measured value, but retains its B-form hybridized structure, whereas A-form DNA converts to the bent B-DNA structure during the simulation, and thus is not stable. After some initial uncertainty about this issue, experiments in the Mirkin group support these results. However, this stimulated new work in the Mirkin group where ethanol was added to the DNA-linked structures, creating conditions that favor A-form DNA. This led to the recent discovery of a large change (by as much as 75%) in lattice spacing that is correlated with a counterion condensation process.[9] It remains to be seen if A-form DNA is involved, but counterion condensation is an important result that provides new directions of research in this area.

**Schatz** and **Nguyen** have investigated the behavior of trebler-linked nanoparticle assemblies where the linear DNA duplex is replaced by molecules in which several DNA strands are attached to an organic molecule to give multiply branched linkers. Coarse Grained Molecular Dynamics (CGMD) simulations have been used to learn about the differences between duplex and trebler linkers,[10] and it was found that employing treblers introduces a high density of binding region in a non-uniform manner. Treblers can be especially advantageous for larger AuNPs, where the surface curvature prevents high loading densities, to enable to synthesis of higher quality crystals from these larger particles.

**Schatz** and **Rosi** have collaborated in studies of peptide amphiphile aggregation into ribbons and other helical structures.[5-6] While there was very good success in modeling the optical properties of gold and silver particles that were grown on the edges of the ribbons (i.e., leading to chiral nanoparticle helices), modeling the ribbon formation itself was found to be quite challenging.

However recently **Schatz** developed a molecular dynamics model that produces ribbon structures from **Rosi**'s peptide amphiphile (Figure 10) and the resulting ribbon is in very good agreement with experiment.

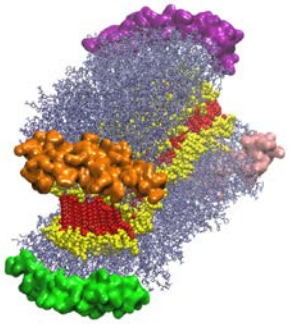

**Figure 10. Structure of a segment of a peptide amphiphile ribbon structure, as obtained from all-atom simulations.**

In order to further study crystal growth using theoretical approaches, **Olvera** introduced a colloidal model to simulate superlattice crystallization, as explicit DNA chains are computationally expensive to model. To do this, an effective interaction between each pair of nanoparticles, with implicit DNA chains was created (Figure 11). Two versions of this have been made, with different assumptions. The first, assumes that the number of DNA binding events can be approximated by the volume overlap of the DNA sticky end shell and that repulsion due to charge can be calculated from Poisson-Boltzmann theory (PB).[11] The second model uses the explicit DNA chains model to calculate the hybridization energy and uses a renormalized PB model to calculate charge interactions.[12]

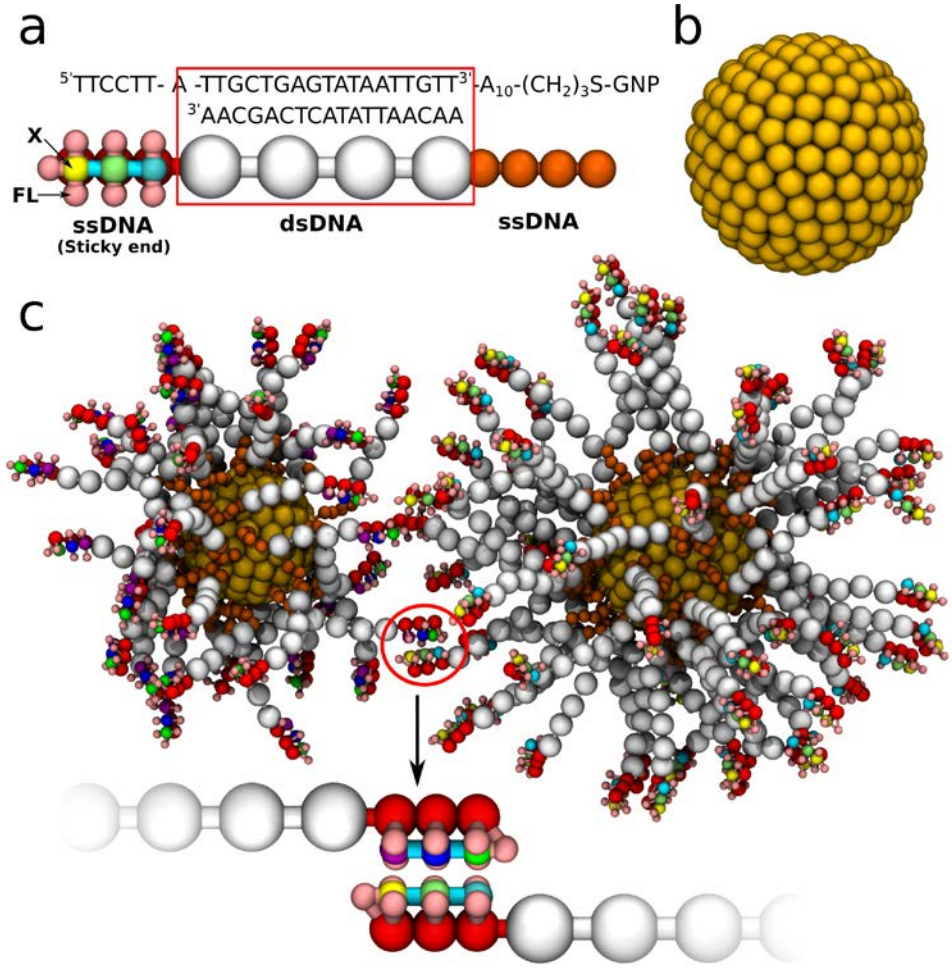


**Figure 11. Schematic of the coarse-grained model for the DNA chain and sequence (a) and for spherical nanoparticle core (b). Two DNA-nanoparticles (c) with a 8nm gold core and 40 DN chains (left) and with a 10nm core and 60 DNA chains (right).**

By using this kind of model, we were able to look at larger scale dynamics of the system.[11] For instance, we investigated crystal growth and coalescence of grains at constant temperatures close to the melting point. These simulations have shown, consistent with experiments, that we first form single crystal grains that grow with a well-known parabolic growth. At later stages, the grains coalesce by a process called grain rotation induced coalescence, that is, the grains that are coalescing form a neck, then rotate around it until their lattices match. Coarsening of the neck follows this process. Overall, coalescing growth is much slower than the initial parabolic growth. Concurrently, crystal growth using a slow-cooling method was investigated.[12] By decreasing the temperature slowly from slightly above the melting point of the system to slightly below the melting point, a single crystal without any coalescence is formed. This leads to single crystal formation that shows the geometric Wulff shapes, an agreement with experimental observations. Moreover, we have shown that the Wulff shape can be predicted by either simple broken-bond models or explicit DNA chain calculations. In order to obtain the equilibrium Wulff shape the bulk crystal energy and the energy of the crystal when a facet is exposed due to the kinetic nature of the hybridization bonds was calculated.[13] It was found that small departures from equilibrium shapes can be expected for small crystals due to thermal fluctuations.[14] These differences become smaller as the crystal grows, eventually reaching the usual Wulff shape construction.

In addition to theoretical studies of spherical nanoparticle crystallization, the use of anisotropic nanoparticles was considered in order to enforce specific bond order arising from directional DNA interactions dictated by particle shape. For instance, one would expect a cube to have 6 neighbors due to its 6 faces. The crystallization of triangular prisms, which form 1D assemblies as a result of their large aspect ratio has been studied.[15] A noticeable difference in these calculations is that the effective persistence length of tethered dsDNA on flat surfaces is greatly enhanced. The main finding in this simulation of DNA coated prisms is that for DNA lengths greater than the typical prism dimension, all orientational order is lost and the prism starts behaving as DNA coated spheres. We also studied regular polyhedrons (cubes, octahedra, rhombic dodecahedron) expecting the same kind of transition from face-to-face packing to spherical packing.[16] This was observed for both octahedra and rhombic dodecahedra, with orientational conformation lost in the transition, as observed for prisms. However, for cubes we observed a transition from the face-to-face packing (simple cubic) into a symmetry-broken lattice (body centered tetragonal), with oriented cubes (see Figure 12). This was confirmed experimentally both in SAXS and by electron microscopy. This body-centered tetragonal lattice transitions into a spherical packing lattice slowly as the DNA length is further increased. This symmetry broken regime was linked to DNA surface configuration as the DNA shell becomes polarized in this regime, which can be controlled by changing DNA surface linkers. While this has yet to be experimentally observed, we have shown that precise control of the surface DNA would enable creating oriented close packed structures, as well as oriented monoclinic or triclinic crystals.

The structure and functionality of nanoparticles functionalized with DNA are intricately coupled to the counterionic layer that surrounds them, and work done in the **Bedzyk** group focuses on understanding this interplay. In the context of this MURI, many unique properties of PAE such as the resistance against nuclease degradation, and the cooperative melting behavior in PAE assemblies are attributed to the high local concentration of cationic counterions in the DNA corona. A first step towards a mechanistic understanding of these phenomena is experimental deduction of the distribution of counterions surrounding PAE.

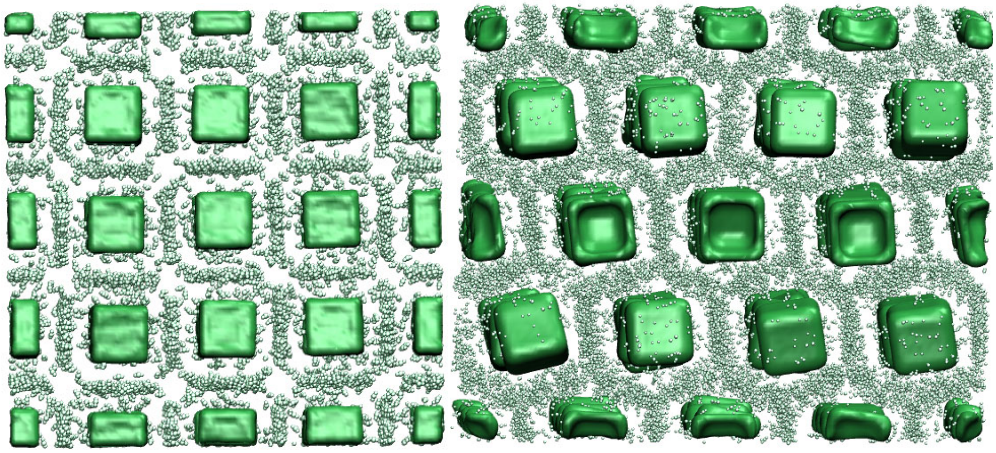

**Figure 12. DNA sticky ends in the (100) plane of cubes in a. SC lattice and b. BCT lattice. Shape of the DNA shell around individual cubes is different in the two lattices, which would have to be captured by a colloidal potential.**

In principle, Anomalous Small Angle X-ray scattering (ASAXS) is the ideal tool for extracting the counterion distribution surrounding DNA-coated nanoparticles with nm-scale resolution in an assumption-free manner. ASAXS relies on the reduction in the scattering power [$Z + f'(E)$] of an atom/ion when the X-ray energy ($E$) is close to the binding energy of a core shell electron. Here, $Z$ is the number of electrons associated with the atom/ion and $f'$ is the dispersive correction term. $Rb^+$ (Z = 36) is ideally suited for ASAXS because its $K$ absorption edge $E_k$ = 15,200 eV is readily accessible at synchrotron sources and is sufficiently high to penetrate water. By measuring, the subtle changes in the $E$-dependent scattered intensities from the DNA coated proteins in a RbCl solution it was possible to extract the counterion distribution.

In addition to investigating counterion distributions in PAE systems, work in the **Bedzyk** group has also focused on the use of X-ray techniques to investigate the mechanisms of various anisotropic nanoparticle syntheses, complementing experimental and theoretical anisotropic particle assembly work in the **Mirkin** and **Olvera** groups respectively. Through use of anisotropic nanoparticles, valency was introduced as a tunable parameter in PAE assembly systems.[17] Yet the use of such particles as PAE building blocks requires the synthesis of anisotropic nanoparticle cores that are monodisperse in both size and shape. One method that has proven successful to create monodisperse anisotropic nanoparticles is the under-potential deposition synthesis of Au nanostructures.[18] As a test case, the use of trace Ag in the synthesis of Au nanorods was investigated.[19]

Although Ag has been shown to increase nanorod yield, monodispersity and aspect ratio, the exact role that Ag plays in the synthesis and where it is distributed in the nanorods remains elusive. This makes it difficult to extend these successful methods to additional systems, in order to extend the library of anisotropic nanoparticle PAE building blocks. Further, in order to create functional PAEs, it is essential to find methods to coat the nanoparticle building blocks with a dense layer of oligonucleotides. This proves challenging in particular for the case of anisotropic nanoparticles, which often use large, strong-binding ligands which make the Au surface less accessible to the traditional gold-thiol chemistry.[17]

To better understand how these functionalization challenges could be overcome, X-ray absorption fine structure (XAFS) was made sensitive to the nanoparticle surface by using sufficiently small nanoparticles (~1.8 nm), for which a majority of their atoms are comprised of surface atoms. In this way, surface contributions become easily observable, as observed from the

raw spectra (see appendix). The X-ray Absorption Near Edge Structure (XANES) region of the spectrum is sensitive to changes in the electronic structure of the Au atoms. Most notably, the intensity of the peak after the edge (white line peak) is inversely proportional to the d-orbital occupancy.[20] This means that the higher the intensity of the white line peak, the greater the positive charge that has been induced on the Au surface atoms. Following this trend and comparing with the bulk Au spectrum ($Au^0$), we observe that the surface atoms in the CTAB-coated particles have a slight partial negative charge, while the surface atoms in the thiol-coated particles have a slight positive charge.

In order to investigate how CTAB binds so strongly to the nanoparticle surface, despite not inducing a significant charge on the Au surface atoms, ab-initio EXAFS analysis was conducted, in order to draw quantitative conclusions concerning what type of atom binding and at what distance from the Au surface atoms. The way in which CTAB binds to Au nanoparticle surfaces was not known previously.[21] Through EXAFS analysis, we determine that Br atoms do indeed coordinate at close proximity (less than 3 Å) from the Au surface atoms. Yet close coordination from the $CTA^+$ portion of the molecule screens the charge, such that the average charge on the Au surface atoms is close to neutral. This complex configuration and effective charge screening enables CTAB to bind strongly to the Au surface, such that the bilayer itself is also stable, making it particularly difficult to remove the CTAB, as the CTAB bilayer structure must be significantly disrupted. In future studies, this information will be used to develop additional methods to successful functionalization of anisotropic Au nanoparticles coated with CTAB and other similar strong-binding surfactants that have traditionally proven difficult.

One major advantage of programmable assembly is the ability to use a variety of functional building blocks as PAEs. One type of functional particle that is of interest due to their tunable optical properties is that of AgAu alloys.[22] In order to investigate the mechanism behind the synthesis of AgAu alloy nanoparticles, a common strategy was employed, which made use of polycrystalline citrate-capped Ag nanospheres as sacrificial templates in the creation of AgAu alloy nanoparticles of varying composition based on titration with $HAuCl_4$ of varying amount. Previously, this reaction has been described as Galvanic exchange, which makes use of a 3:1 Ag:Au ratio based on the preferential reduction of $Au^{3+}$ onto the Ag template at the expense of Ag oxidation.[23] This results in an alloy nanoparticle that is both hollow and porous in morphology.

Small angle X-ray scattering (SAXS) provides us with global insight into the evolution of nanoparticle morphology. Analysis from modeling of the SAXS patterns reveals that the overall size of the nanoparticles does not change significantly throughout the reaction, rather the hollow core size increases as the alloy shell size decreases. XAFS at the Au $L_3$ and Ag K edges was used to investigate the transformation mechanism and structure of the AgAu alloy at the atomic level. In literature, it has been presumed that a homogeneous alloy forms during the transformation process.[23] Yet, we find that this is not the case. Even when the nanoparticles are primarily Au, still the Ag atoms are mostly coordinated with Ag. This suggests that the Ag and Au atoms exhibit local clustering, which has important implications on the nanoparticle optical and catalytic properties.

Through combining our X-ray results with those previously observed experimentally or theorized computationally in literature, an outline of the a mechanism for the transformation of Ag nanoparticles into AgAu nanocages is proposed: (1) The reaction begins with 20 nm citrate-capped Ag nanosphere templates; (2) Au initially deposits and plates at grain boundaries and other surface defect sites; (3) Pits form on surface due to Au surface diffusion to facilitate Ag dissolution through Galvanic replacement; (4) Pits coalesce into central void in order to minimize surface energy; (5)

Central void expands as additional replacement occurs; (6) Dealloying begins to degrade particles and increase porosity as replacement continues through a combination of plating and Galvanic replacement; (7) Hollowing leads to structural instability and particles deteriorate above ~ 75 % Au. the results of this study will be used to incorporate nanoparticles with optimized optical properties through an Ag functionalization strategy into DNA-programmable assemblies with optical functionality (see Figure 13).

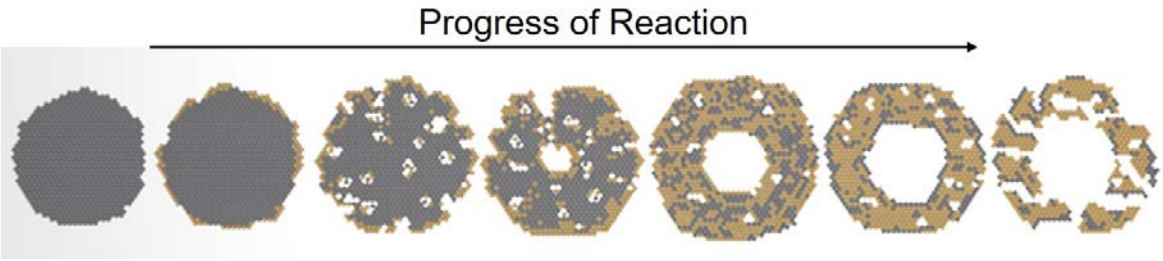


**Figure 13. Mechanism schematic of the formation of AgAu alloy nanoparticles. A pictoral schematic of the reaction mechanism is shown, starting with spherical Ag nanoparticles (left), and ending in AgAu alloy nanoshells (right).**

It has been demonstrated nanoparticles grafted with a dense monolayer of synthetic oligonucleotides can act as building blocks in the synthesis of ordered superlattices with nm-scale control over particle placement in three dimensions. While these PAEs can form highly ordered nanoparticle arrays, the resulting lattices are typically polycrystalline, limited to grain sizes of ~500-2000 nm, with uncontrollable orientations or overall lattice habits. To construct and probe a useful optical material, a single crystal on the order of tens of micrometers or larger must be fabricated, with a controllable orientation relative to a substrate and to other optical components. Polycrystalline body-centered cubic (bcc) (100) and (110) thin films have already been grown on unpatterned DNA-modified substrates, opening the door to the formation of crystals with a fixed location and orientation. Although thin-film assemblies grown in this manner with appropriate annealing display a uniaxial texture (preferential orientation normal to the substrate), they remain polycrystalline with domain sizes similar to those of crystals in solution.

Epitaxial growth, that is, the use of a crystalline substrate to control order and orientation in a growing crystal, is typically a very effective method of transferring large-scale order to materials that would otherwise display amorphous or polycrystalline material growth mechanisms. Nonetheless, prepatterned surfaces have only been used in a limited capacity to direct assembly of DNA-modified nanoparticles. Under this MURI project, a technique was developed to epitaxially grow thin film PAE single crystal superlattices in a manner analogous to that of traditional atomic thin film growth. Electron-beam lithography was used to pattern gold features on silicon; after DNA functionalization, the resulting substrate was roughly equivalent to the first layer of a PAE crystal, and could subsequently be used as a template for solution-phase homoepitaxy.

This process was first investigated with adlayer growth on single-domain 100 square μm templates with regards to defect formation, lattice mismatch, and the role of the templated crystal plane on superlattice orientation. Epitaxial growth of bcc superlattices was effected in a manner similar to that used for preparing polycrystalline thin films of PAEs, but instead of using an amorphous gold substrate, a nanofabricated one resembling a superlattice crystal plane was employed. Specifically, a template was designed and fabricated using conventional electron-beam lithography in poly(methylmethacrylate) (PMMA; Figure 14a). After exposure and development, 3 nm Ti or Cr and 12 nm Au were sequentially deposited, and the PMMA was lifted off. The

fabricated template was then functionalized with 3′-propylthiolmodified DNA, and oligonucleotide linkers with seven base long “sticky ends” were introduced to enable hybridization to PAEs.

For a submonolayer film, three largely distinct adsorption patterns were observed, corresponding to PAE attachment to either one (corner-bound), two (edge-bound), or four (centerbound) DNA-functionalized lithographic features (Figure 14d). This behavior is most easily observed for submonolayer films but also holds true for full monolayer structures. Since the patterned features on the surface are the equivalents of A-type particles in a bcc lattice, center-bound attachment of PAEs corresponds to the continuation of the lattice. Therefore, in this context edge-bound or corner-bound PAEs constitute defects in the growing crystal.

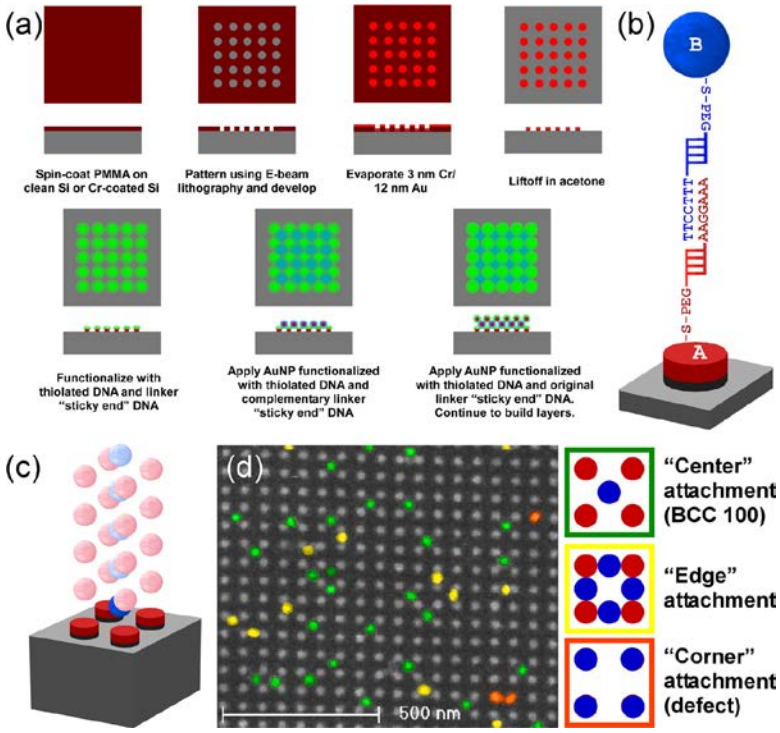


**Figure 14. (a) Template fabrication process. (b) Schematic illustrating the DNA binding scheme between template and nanoparticles or between nanoparticles of opposite types (not to scale). (c) Schematic of an ideal bcc (100) crystal epitaxially grown on a surface. Gold surfaces functionalized with DNA containing A-type single stranded ends are shown in red, and gold surfaces with complementary B-type single stranded ends are shown in blue. Full color illustrates the portion discussed in this work. For clarity, the DNA itself is not included. (d) Submonolayer growth on a bcc (100) template, imaged via SEM, with nanoparticles in false color. Submonolayer growth is shown to better illustrate three types of binding modes: centerbound nanoparticles are colored green, edge-bound nanoparticles are colored yellow, and probable corner-bound nanoparticles are colored orange. The associated schematic illustrates these corner, edge, and center-bound particles. In the schematic, template sites presenting A-type sticky ends shown in red, and deposited particles presenting B-type sticky ends shown in blue.**

To test the flexibility of PAE thin films assembled on lithographically patterned substrates, growth of the originally designed lattice with a lattice parameter of 62 nm on lithographic features of variable distances (57 nm, 59 nm, 65 nm, 68 nm, and 76 nm) was investigated. The amorphous matter in the SEM images is leftover silica from a sol−gel embedding process required to stabilize the superlattices for drying and imaging with SEM. The most notable defects in the compressed lattices were vacancies. In contrast, strained lattices showed a tendency toward increasing numbers of edge-bound nanoparticles (see Figure 15).

Like atomic systems, there are many design parameters that can affect multilayer epitaxy, such as factors inherent to the deposition protocol (e.g. thermal annealing temperature) and factors dictated by PAE design (e.g. DNA hybridization strength). However, unlike atomic epitaxy where only the deposition protocol can be modulated, parameters related to the individual PAE building

blocks can be precisely controlled as a function of DNA, particle, or substrate pattern design. Under this MURI project, the deposition of particles onto templated substrates via far-from-equilibrium conditions (i.e. low growth temperature) was studied first to understand the effectiveness of the EBL-patterned template itself as a driving force for multilayer epitaxy. In this system, when conducting templated PAE deposition at 25 °C, initial layers conformed epitaxially to the substrate, but subsequent layers transitioned to a kinetically roughened, glass-like state (Figure 16a). The relative degree of epitaxy ($X_A$) at each layer was determined by comparing the SAXS intensity of the spots from the (110) peak of the epitaxial PAEs and the intensity of the diffuse ring, where an $X_A$ value of 1 indicates complete epitaxy of the PAEs; the value of $X_A$ decays from 0.99 to 0.88 after 5 layers, and to 0.65 at 10 layers. This was corroborated by the FIB-SEM cross-sectional images, which showed that the first few layers of all samples are indeed epitaxial, up to a critical layer number of ~4, with PAEs above the critical layer adopting a kinetic, glassy state (Figure 16a bottom). This is a morphological transition commonly observed in atomic thin films, which exhibit temperature-dependent surface roughening when the adsorption rate is faster than the reorganization rate. Similarly, PAEs adsorbed at low temperature were stuck in kinetic traps, leading to an accumulation of defects in the film, which increases the surface area available for the subsequent NPs to bind. This results in amorphous, rough films; the root-mean-squared roughness ($R_{RMS}$) increases by 140% from 2 to 10-layer deposited films. These data clearly show that the EBL template does serve as a strong driving force for epitaxy, but this force rapidly decays with increasing layer number when lattices are assembled at non-equilibrium conditions.

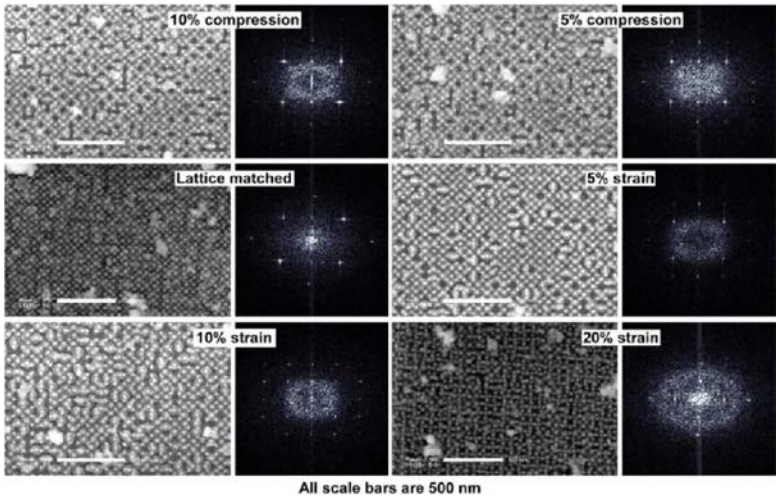


**Figure 15. SEM images of monolayer bcc (100) crystals grown on epitaxial templates with −10%, −5%, +5%, +10%, and +20% strain, respectively, as indicated, and two-dimensional fast Fourier transforms of the images, center point removed and cropped to feature lower frequencies. The amorphous matter in the SEM images is left over silica from a sol−gel embedding process required to stabilize the superlattices for drying and imaging with SEM.**

It is possible to reorganize thin films into more thermodynamically preferred configurations by adding thermal energy. This process was achieved by first depositing 5 and 10 layers at 25 °C and then heating the sample slightly below the film's melting temperature ($T_m$, the temperature at which the superlattice dissociates). Interestingly, in the process of determining the films' $T_m$, it was observed that they exhibit thickness-dependent melting point depression, analogous to atomic thin film systems. The thermal stability of the film, measured by monitoring lattice decomposition using SAXS, showed a concomitant increase with thickness, due to the decreasing surface-to-volume ratio, as described by Lindemann's criterion and the Gibbs-Thomson relationship. Upon annealing the samples at ($T_m$–2) °C, the 5-layer film became crystalline and epitaxial while retaining the same height and $R_{RMS}$. On the other hand, the 10-layer sample became crystalline, but not epitaxial (Figure 16b). This is most likely due to the fact that the previously observed critical layer thickness for epitaxy is ~4, indicating that, in the 5-layer

sample, only the top-most layers of nanoparticles were disordered. The differences in epitaxy for these two samples mirror previous findings for non-epitaxial PAE systems, in which post-assembly annealing induces crystallization, but grain boundaries are difficult to remove once formed.

The greatest degree of ordering in thin films can be achieved when the entire deposition process occurs under near-equilibrium conditions. To achieve this effect in the PAE system, each layer was deposited at an optimized growth temperature, ($T_m$–4) °C. With this method, nearly perfect Frank-van der Merwe (layer-by-layer) growth was observed, with films remaining epitaxial ($X_A$ = 0.99) far beyond the critical layer thickness of room temperature growth (Figure 16c). Film cross-sections examined with FIB-SEM show smooth surfaces with an absence of kinetic roughening; the $R_{RMS}$ of the 10-layer film is 51% less than that of the equivalent film assembled at 25 °C. Film height increases linearly with deposition layer, indicating that deposition occurred under equilibrium conditions. Both GISAXS and SAXS confirmed that the film is well-ordered over a large area and nearly completely epitaxial with the patterned template (Figure 16c middle). Notably, a loss of radial broadening in the SAXS pattern, corroborated by FIB-SEM, indicates that as the film grows from 2 to 5 layers, the stability of the PAE network increases to such a point that the particles become locked within a single domain. The appearance of thin lines of diffuse scattering between the peaks originates from the vibrational motion of the particles. This equilibrium growth condition was therefore able to create a crystalline film of well-defined and arbitrary crystal habit that is epitaxial over a domain of 500 μm (Figure 16).

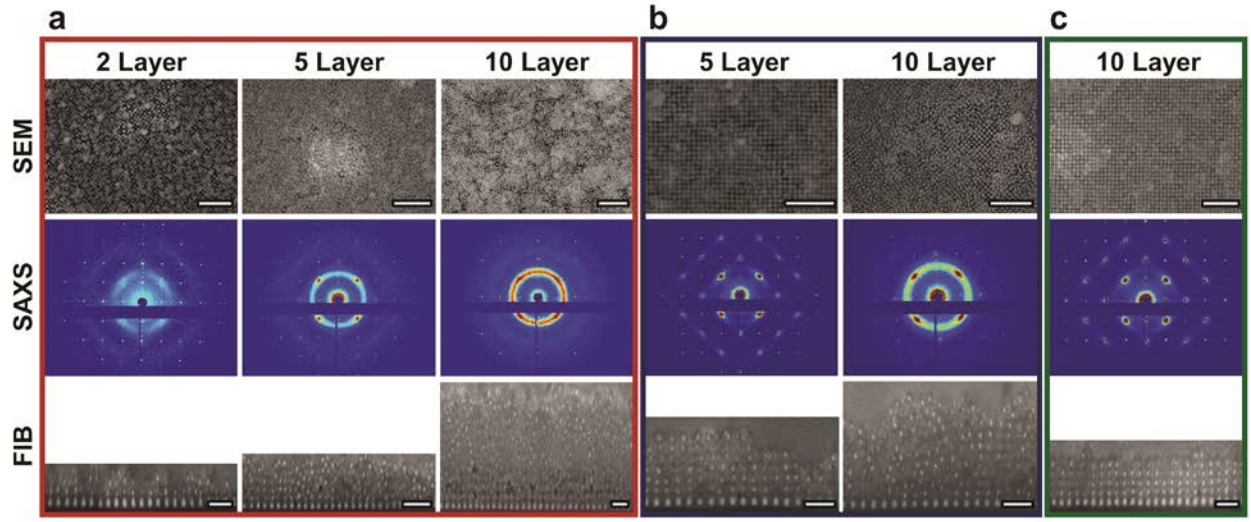


**Figure 16. SEM, SAXS, and FIB-SEM characterization of PAE thin films. a) 2, 5, and 10-layer DNA-NP thin films assembled at 25 °C exhibit kinetic roughening and non-epitaxial growth beyond 4 layers of deposited PAEs. b) 5 and 10-layer DNA-NP thin films assembled at 25 °C and thermally annealed after the full deposition process demonstrate enhanced ordering, but only the 5-layer sample is fully epitaxial since only PAEs that are close to the initial 4 epitaxial layers experience sufficient driving force to align with the patterned template. c) A 10-layer DNA-NP thin film where each layer is assembled at an elevated temperature; this process produces smooth, crystalline thin films fully epitaxial with the patterned substrate. Scale bars for SEM and FIB-SEM are 500 nm and 200 nm, respectively.**

In principle, the design rules for DNA-directed assembly of superlattices represent the first of potentially many examples of composite materials that can be made via self-assembly, as the forces that dictate the assembly process (although they are precisely controlled via DNA base sequence) are not specific to oligonucleotides. In principle, any nanoparticle and polymer-based system with numerous reversible interactions at a programmable distance from the particle surface

should be capable of driving the formation of ordered arrays of inorganic materials within an organic matrix. This is an important note, as the physical characteristics of such composite materials are dictated by not only the chemical composition, but also the spatial configuration of each constituent phase. A major challenge in nanoparticle-based composites is developing methods to precisely dictate particle positions at the nanometer length scale, as this would allow for complete control over nanocomposite structure-property relationships. Under this MURI, a new class of building blocks was developed called nanocomposite tectons (NCTs), which consist of inorganic nanoparticles grafted with a dense layer of polymer chains that terminate in molecular recognition units capable of programmed supramolecular bonding. By tuning various design factors including particle size and polymer length, the supramolecular interactions between NCTs were used to controllably alter their assembly behavior, enabling the formation of well-ordered body centered cubic superlattices consisting of inorganic nanoparticles surrounded by polymer chains. NCTs therefore presented a modular platform enabling the construction of composite materials where the composition and three-dimensional arrangement of constituents within the composite were independently controlled.

The first example of a NCT was demonstrated by grafting gold nanoparticles (AuNPs) with polystyrene (PS) chains that terminate in molecular recognition units with complementary hydrogen bonding motifs (diaminopyridine, DAP, and thymine, Thy). Gold nanoparticles provided a sensitive spectral probe for particle assembly and were easily functionalized via gold-thiol chemistry, while polystyrene was synthesized with a wide range of molecular weights and low polydispersity using controlled radical polymerization techniques such as atom transfer radical polymerization (ATRP). Complementary hydrogen bonding via the DAP and Thy units provided a simple means of controlling particle interactions by modulating temperature, since hydrogen bonds dissociate upon addition of heat.

Two clear trends were observed when temperature melt experiments were performed. First, when the polymer molecular weight was held constant, the $T_m$ increased with increasing particle size (Figure 17a). Conversely, when the particle diameter was kept constant, the $T_m$ drastically decreased with increasing polymer size (Figure 17b). Importantly, because the NCT assembly process was based on dynamic, reversible supramolecular binding, it was possible to drive the system to an ordered equilibrium state where the maximum number of binding events occurred. It was hypothesized that, despite the inherently polydisperse nature of both the particle cores and the polymer ligands, ordered arrangements represented the thermodynamically favored state for a set of assembled NCTs. When packing NCTs into an ordered lattice, deviations in particle diameter were expected to generate inconsistent particle spacings that decreased the overall stability of the assembled structure. However, the inherent flexibility of the polymer chains -allowed the NCTs to adopt a conformation that compensated for these structural defects. As a result, an ordered arrangement was still predicted to be stable if it produced a larger number of DAP-Thy binding events than a disordered structure generated. The bcc structure was observed for multiple combinations of

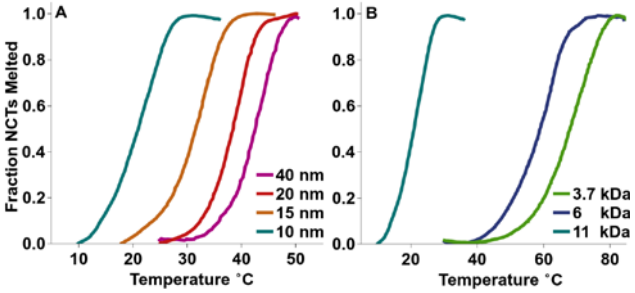


**Figure 17. Thermal study of complementary NCT mixtures with (A) constant polymer molecular weight (11 kDa) and varying NP diameter; (B) constant particle diameter (10 nm) varying polymer molecular weights.**

particle size and polymer length (Figure 18), indicating that the nanoscopic structure of the composites were controlled as a function of either the organic component (via polymer length), the inorganic component (via particle size), or both, making this NCT scheme a highly tailorable method for the design of future nanocomposites.

During the past five years, the **Nguyen** group leveraged its expertise in the synthesis and assembly of small molecule-DNA hybrids (SMDHs) toward the synthesis of programmable atom equivalents (PAEs). SMDHs comprise oligonucleotides covalently linked to an organic "core" where the number and geometry of reactive sites dictate the precise quantities and locations of conjugated DNA strands. This absolute control over strand quantity and orientation is an important distinction when compared to DNA-nanoparticle conjugates (DNA-NPs), which inherently have a distribution of strands on their surfaces. A major portion of the efforts by the **Nguyen** group took advantage of this well-defined parameter to synthesize discrete SMDH structures in a modular fashion. In addition, they focused on interfacing SMDHs with DNA-NPs to utilize the properties of both types of conjugates.

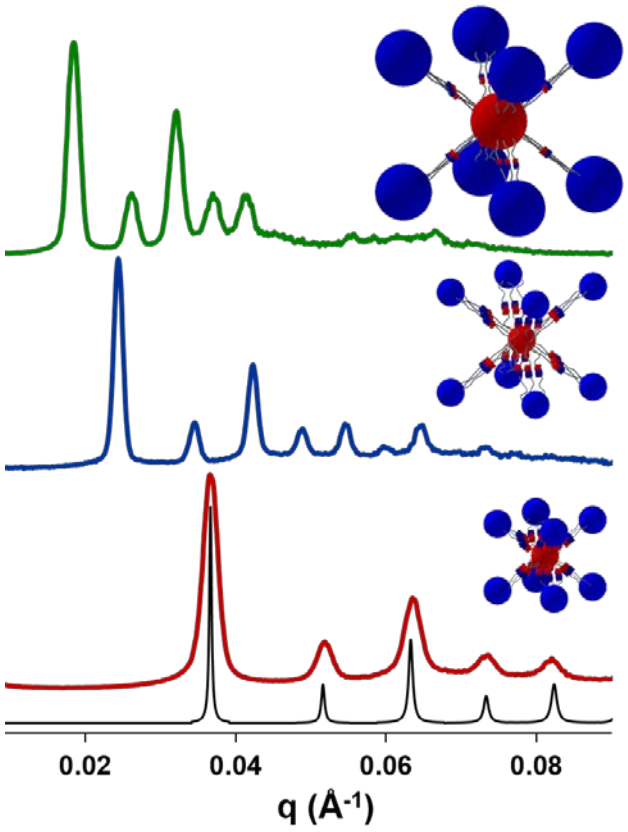


**Figure 18. SAXS data showing NCT assembly into ordered bcc superlattices: (green trace) 20 nm AuNPs and 11 kDA PS; (blue trace) 10nm AuNPs and 11 kDA PS; (red trace) 10nm AuNPs and 6 kDA PS; (black trace) predicted SAXS pattern for a perfect bcc lattice. Insets show the unit cell for each lattice drawn to scale.**

First, **Nguyen** and coworkers developed a methodology for the synthesis of multiply functionalized (mono, di, tri, and tetra) small molecule-DNA hybrid building blocks through a robust, high-yielding, and versatile solid-phase synthesis in a single reaction.[24] As an example, a rigid tetraazide core is conjugated with alkyne-functionalized DNA strands that were synthesized on controlled pore glass (CPG) beads using copper (I)-catalyzed "click" chemistry. Upon cleavage from the CPG beads, each SMDH species was purified and isolated using reversed-phase high-performance liquid chromatography (Figure 19). This

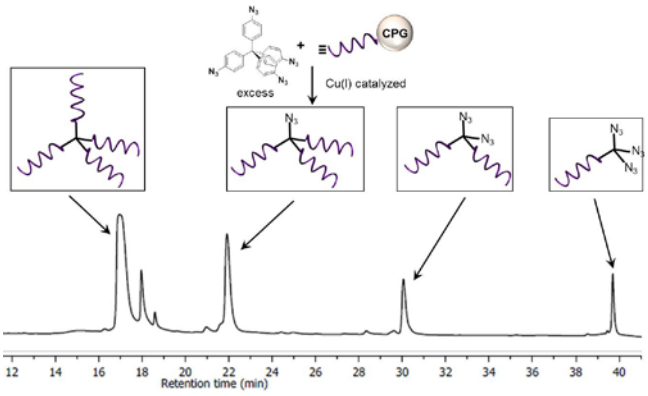


**Figure 19. Analytical HPLC trace of reaction mixture for mono-, di-, tri-, and tetra-functionalized SMDH building blocks made using "Click" chemistry with alkyne-functionalized DNA strands on a CPG.**

solid-phase strategy favored the formation of $SMDH_4$ and $SMDH_3$ in high yields while $SMDH_2$ and $SMDH_1$ were preferentially obtained using solution-phase methods.

Next, the **Nguyen** group demonstrated a strategy that dramatically improved the yield of discrete, well-defined DNA cage dimer structures from the assembly of complementary $fSMDH_3$ comonomers comprised of highly flexible tris(oxypropyloxymethyl)methyl organic core **1** (Figure 20) surrounded by three DNA arms with variable lengths (9, 15, and 24 bases).[10] The highly flexible core **1** greatly biased the assembly process to favor caged dimers, even at very high $fSMDH_3$ concentrations (32 μM or ~100 μM DNA). Oligomers and ill-defined networks did not form in the assembly of 9-$fSMDH_3$ comonomers with 9-base DNA arms and the assembly of 15-$fSMDH_3$ comonomers with 15-base DNA arms yielded mostly dimers. Higher-order materials (tetramers and larger oligomers) only form in appreciable amounts when the DNA arms of the $fSMDH_3$ are lengthened to 24 bases, as shown by both experimental studies and molecular dynamics (MD) simulations.

In addition, **Nguyen** and coworkers demonstrated that the assembly of complementary $SMDH_3$ comonomers were significantly affected by core flexibility and geometry. To this end, they carried out a comparative study on the assembly of SMDHs derived from the highly flexible tetrahedral trivalent core **1** as well as the more-rigid pyramidal and trigonal cores **2** and **3**, which have different branch-center-branch angles (107º for the pyramidal core, and 120º for the trigonal planar core) due to their different geometrical arrangements (Figure 20).[25]

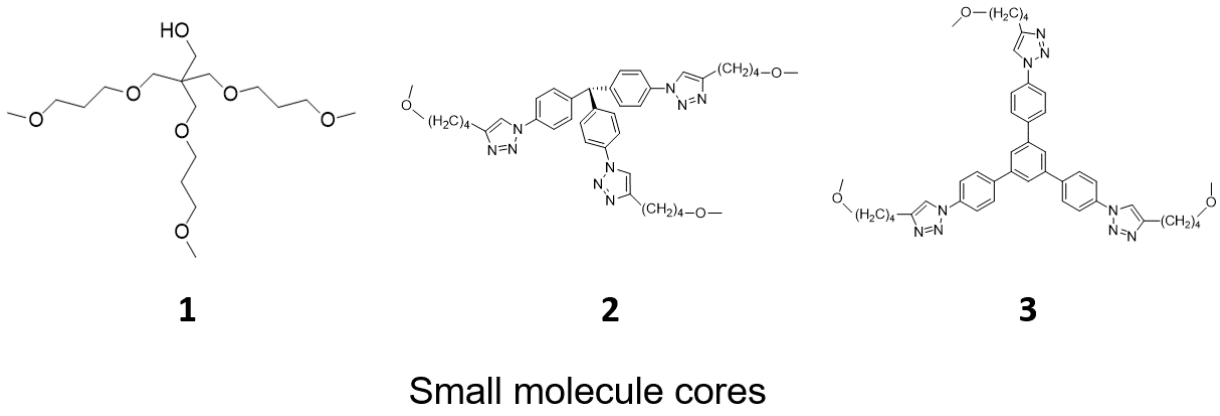


**Figure 20. Small molecule organic cores used in SMDH syntheses: highly flexible core 1, rigid pyramidal core 2, and highly rigid trigonal planar core 3.**

Interestingly, the different geometries of cores **2** and **3** also manifested into significant differences in assembly formation. At the same $SMDH_3$ concentration ($[SMDH_3]$ = 32 μM), the assembly of $pyrSMDH_3$ comonomers gave a higher number of caged dimers and small networks (up to octamer; 63%) than large-oligomer networks (≥ nonamers; 37%); whereas the assembly of $tpSMDH_3$ comonomers resulted in a higher population of large-oligomer networks (60%). This behavior was attributed to the difference in the geometry and angle of branch-center-branch of cores. The pyramidal core **2** has a bent geometry and smaller angle, which brings the DNA arms closer to each other, which facilitated the formation of smaller networks. On the other hand, the DNA arms of the trigonal planar core **3** were farther from each other, which made it easier for them to form larger assemblies.

In collaboration with the **Schatz** group, **Nguyen** and coworkers developed a greatly improved CGMD model with an extended parameter set that can accurately forecast the experimentally

observed population distributions of $SMDH_3$ assemblies over a broad range of DNA concentrations as a function of the overall flexibility and geometry of the organic core.[10, 25] Consistent with the experimental results, CGMD simulations demonstrated that $fSMDH_3$ comonomers with the highly flexible core **1** predominantly formed supramolecular cage dimers (larger networks rarely observed). In contrast, $pyrSMDH_3$ or $tpSMDH_3$ comonomer pairs, with the more-rigid cores **2** or **3**, were assembled into a number of species across the range of explored concentrations. Moreover, the CGMD model accurately predicted the effect of the hydridizing DNA arm length on $SMDH_3$ assembly behaviors. A subtle interplay between the intrinsic rigidity of the organic core and the flexibility afforded by incorporating $T_n$ spacer units between the hydridizing DNA arms and the organic core was found.

The **Nguyen** group also developed spherical nucleic acid-based polymeric nanoparticles that were easily synthesized through the simple hybridization of two complementary tetrahedral small molecule-DNA hybrid (SMDH) building blocks without the need for an underlying template or scaffold (Figure 21).[26] The sizes of these particles were tailored in a facile fashion by adjusting assembly conditions such as SMDH concentration, assembly time, and NaCl concentration. Notably, these novel particles were stabilized and transformed into functionalized spherical nucleic acid (SNA) structures by the incorporation of capping DNA strands conjugated with functional groups. These results demonstrated a systematic, efficient strategy for the construction and surface functionalization of well-defined, size-tunable nucleic acid particles from readily accessible molecular building blocks. In collaboration with the **Mirkin** group, **Nguyen** and coworkers synthesized a new linker system comprised of either two- or three-armed trebler sticky ends to drive crystal assembly instead of the single-connection DNA linkers that are traditionally used to construct DNA-linked SNA superlattices.[27] Both di- and trivalent DNA linkers were readily incorporated into the oligonucleotide shells that define DNA-NPs and behaved as double- and triple-bond analogs of the traditional "single-bond", "linear" design in PAE-based assembly of superlattices. These multivalent bonding motifs enabled the change of "bond order" between particles in PAE assembly, effectively modulating the interparticle "bond strength". In addition, the improved accessibility of the hybridizing DNA strands between neighboring particles, due to either multivalency or modifications to increase strand flexibility, gave rise to superlattices with less strain in the crystallites compared to traditional "linear" linker designs. These structural differences manifested in the melting behavior of DNA-NP aggregates, where the samples made of double and triple DNA "bonds" showed elevated melting temperatures ($T_m$ increases by 5 to 9 °C) and sharpened melting transitions when compared to "single" bonds.

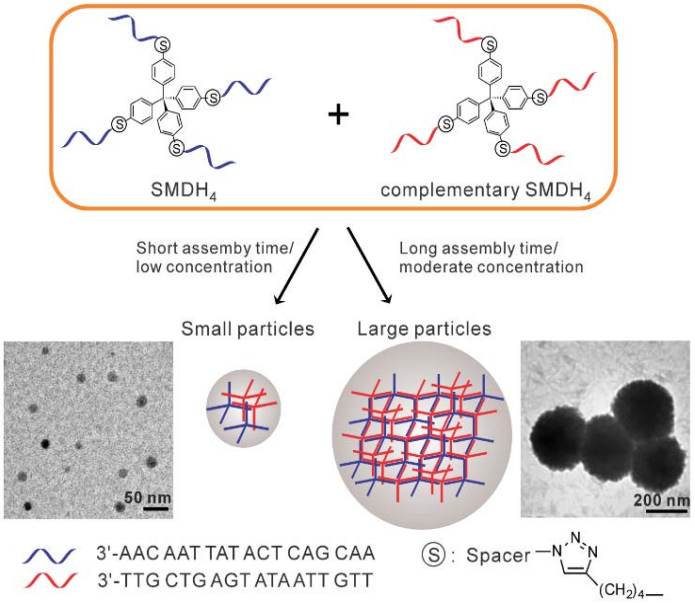


**Figure 21. The assembly of nucleic acid-based polymeric nanoparticles from $SMDH_4$ and its complementary partner. Size-tunable particles can be obtained by slow (~0.2 °C/min; right) or fast (~10 °C/min; left) cooling of a "hot" assembly solution (total [DNA] = 15 μM, T = 90 °C), respectively.**

Notably, the increased availability and number of binding modes provided a new variable that allowed previously unobserved crystal structures to be synthesized, as evidenced by the formation of a novel $Th_3P_4$ superlattice.

A fundamental study was carried out in collaboration with the **Mirkin** group to gain insight into the thermodynamics of DNA-NP crystallization of superlattices that focused on the role of flexibility in the DNA linker design. At the beginning of the MURI project, almost all observed crystalline phases for PAE-based superlattices were predicted/rationalized based on the principle that *the thermodynamic structure* was the *one that* maximized the *nearest neighbor connections*. As a representative example, a self-complementary DNA-NP system was expected to form a face-centered cubic (fcc; 12 nearest neighbors) superlattice as this symmetry maximizes the number of DNA connections. While such a guiding principle allowed for high levels of predictability when designing a PAE superlattice, it primarily focused on the enthalpic contributions to the overall free energy of crystallization and minimized entropic contributions. Under the MURI support, this knowledge gap was remedied: the use of either long, flexible linkers or small inorganic cores w "force" the aforementioned fcc-crystallizing system to form a body-centered cubic (bcc; 8 nearest neighbors) superlattice while keeping the same self-complementary sticky ends. Such unusual assembly behavior was attributed to the ability of flexible strands to access additional configurational states, resulting in significant entropic contributions to the overall free energy of crystallization. **Olvera de la Cruz** and coworkers confirmed this notion through coarse-grained molecular dynamic simulations in which the differences in strand length and flexibility were accurately modeled.

In a collaborative project with the **Rosi** group, **Nguyen** and coworkers developed a novel set of peptide-oligonucleotide chimeras, building blocks with two bioprogrammable materials bridged across an organic core. With this highly modular platform, many design parameters were independently tuned such as DNA length, secondary structure (i.e., duplexed or single-stranded), as well as molecular connectivity (Figure 22) and subsequently correlated with observed assembly morphology. As an initial proof of concept, a rigid 4,4'-diethynyl-1,1'-biphenyl ditopic organic core was used to link the DNA and peptide moieties in a one-to-one ratio. Covalent attachment of the oligonucleotide was achieved using an azide-alkyne cycloaddition reaction and two different azide-modifications to the oligonucleotide, providing two different types of attachment flexibility to the system (Figure 22, last panel). Both of these approaches enabled a range of DNA sequences to be modified with two types of molecular connectivity when conjugated to the biphenyl core and offered levels of flexibility for the chimeras upon assembling into superstructures with different morphologies (1-D fibers, spherical vesicles, etc.)

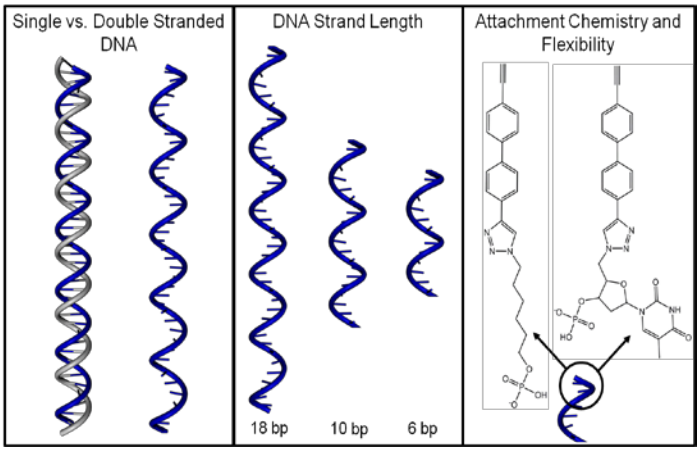


**Figure 22. Illustration of the wide parameter space available to the oligonucleotide portion of these peptide-oligonucleotide chimeras.**

One goal during the funding period was to develop methods for using peptide-based molecular constructs to direct the synthesis and assembly of discrete zero dimensional nanoparticle

superstructures (e.g. spherical nanoparticle assemblies) and 1-dimensional linear nanoparticle assemblies (e.g. helical nanoparticle assemblies). The peptide constructs served a dual purpose: they associated to the inorganic nanoparticle surface and they assembled with one another into hierarchical structures. In this way, they directed the assembly of nanoparticles and the nanoparticle assembly adopted the structure of the peptide assembly. The aim was to develop a fundamental understanding of how the adjustment of the molecular constitution of peptide-based molecular construct could influence and affect the morphology, structure, and properties of the nanoparticle superstructure. Specific aims included controlling nanoparticle dimensions, controlling superstructure metrics, controlling nanoparticle composition, and develop a basis to understand how the underlying molecular structure of a peptide assembly translated into the structure of the nanoparticle assembly. During the course of the funding period additional projects were developed, notably a study aimed at creating oligonucleotide-peptide constructs, studying their assembly behavior, and understanding the key factors that influenced their assembly.

Hollow spherical nanoparticle superstructures represent an important class of nanoparticle assemblies that garnered interest as metamaterials, nanoscale reactors, and nanoscale capsules. Before realizing the promise of such structures, systematic methods were required to control their assembly by design, to control their diameter (i.e. spherical diameter of nanoparticle superstructure), and to control their composition.

Peptide constructs were designed to direct the assembly of gold nanoparticles into hollow spherical superstructures and synthetic methods were developed to control the diameter of these superstructures.[28] Specifically, $C_6$-AA-$PEP_{Au}$ (A = alanine ; $PEP_{Au}$ = AYSSGAPPMPPF) assembled into vesicular structures in aqueous buffer and directed the assembly of Au nanoparticles into a monolayer shell on the surface of the vesicles. The peptide sequence, AYSSGAPPMPPF, was isolated by Naik and coworkers at the AFRL. The resulting structure was defined as a 'hollow' spherical nanoparticle superstructure. By adjusting parameters such as buffer concentration, peptide concentration, and gold precursor concentration, spherical superstructures with diameters of ~40 nm, ~75 nm, and ~150 nm were prepared (Figure 23). The surface plasmon resonance band for these superstructures red-shifted as the diameter increased, from 545 nm (40 nm), to 670 nm (75 nm), and to 740 nm (150 nm) (Figure 23). The position of these resonances matched what was predicted by theory (**Schatz** group). The 75 nm and 150 nm structures had rather broad extinction profiles that extended into the near infrared (NIR). These studies demonstrated that tuning the conditions for nanoparticle assembly resulted in control over the metrics of the assembly product.

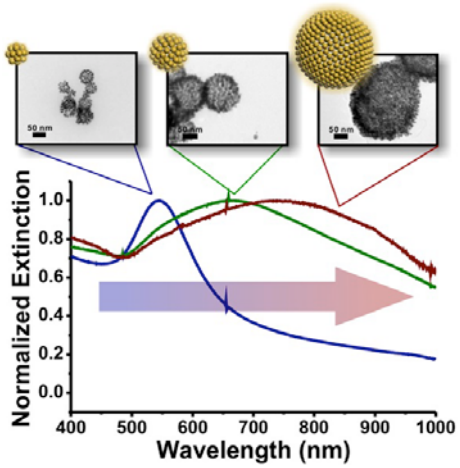


**Figure 23. Hollow spherical gold nanoparticle superstructures of tunable diameter and their corresponding SPR response.**

The cargo storage and release capabilities of the hollow spherical nanoparticle superstructures were investigated, with an aim to understand the stability of the structures in the presence of external species (e.g. enzymes) and under illumination with near infrared (NIR) light.[29] It was envisioned that such structures could be designed to capture and destroy certain target analytes or release certain species upon application of an external stimulus. The enzymatic stability

of these species was studied because their structures depend on the peptide assembly; in the absence of peptides the structures would fall apart. Enzymatic stability is important for any biomaterial that contacts biological fluids containing enzymes, including human sweat, saliva, and blood. It was found that the mid-sized spherical nanoparticles (~75 nm diameter) remained intact in the presence of protease K, while the larger spherical nanoparticles (~150 nm diameter) fell apart in the presence of protease K. It was observed that the mid-sized nanoparticles exhibited a continuous shell of Au nanoparticles, whereas the larger spheres contained some crevices in the Au nanoparticle shell. It was reasoned that protease K could enter the large spheres through these gaps and digest the peptide-based vesicle underneath the nanoparticle shell. It was also shown that large fluorescent molecules could be encapsulated within the mid-sized and larger spherical nanoparticles and that irradiation with NIR light led to degradation of the nanoparticles and caused release of the cargo molecules. NIR irradiation at the surface plasmon band frequency led to a local heating effect that resulted in destabilization of the nanoparticles, presumably through agitation of the peptide-based vesicle that served as the scaffold onto which the nanoparticles were assembled. These studies were the first step toward applying the hollow spherical gold nanoparticle superstructures in an application that required both their structural and physical properties. The study pointed a direction toward using these materials for the triggered release of molecular species.

Helical nanoparticle superstructures are an important class of chiral nanoparticle assemblies. They have the potential to serve as nanoscale circular polarizers, chiroptical sensors, and they represent an important new entry into the metamaterials catalogue. The design, assembly, and control of structural metrics, composition, and chiroptical properties of helical nanoparticle superstructures was a major thrust during the funding period.

Efforts in this area began with exploration of the chiroptical properties of left-handed gold nanoparticle double-helical superstructures. These were prepared using $C_{12}$-$PEP_{Au}$, in which all the amino acids were '*L*' form. The structures exhibited chiroptical activity at ~560 nm, which corresponded to the collective surface plasmon resonance of the assembled gold nanoparticles (Figure 24). Computational models developed by Schatz and coworkers predicted this activity. Helices comprising larger nanoparticles were prepared because computational modeling work predicted that an increase in particle diameter would lead to a concomitant increase in chiroptical signal. Right-handed gold nanoparticle double helices were prepared using $C_{12}$-$PEP_{Au}$, in which all the amino acids were '*D*' form. These helices exhibit roughly equal and opposite chiroptical activity compared to their enantiomer, the left-handed helices (Figure 24). The position and intensity of the plasmonic CD signal was further adjusted by plating the right- and left-handed helices in a coat of silver.[6] The double helices were one of the first nanoparticle superstructures that exhibited a measurable chiroptical response. The work demonstrated that the double helices exhibited

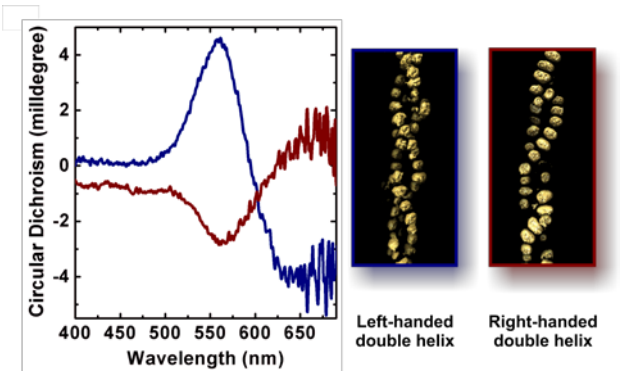


**Figure 24. Left- and right-handed gold nanoparticle double helices and their corresponding CD spectra (blue, left; red, right).**

chiroptical activity and their structures could be systematically modified to adjust and control this activity.

Motivated by Schatz's theoretical modeling and predictions that the strength of the chiroptical response of the gold nanoparticle helices should be inversely proportional to helix pitch, strategies were developed to systematically control the pitch of the helix via design of the peptide conjugate molecule. The number of peptide head groups per aliphatic tail (i.e. peptide conjugate valency) was modified to control the pitch of the assemblies based on the previous model of the peptide conjugate assembly. It was reasoned that increasing the volume of the peptide portion of the conjugate should decrease the pitch; that is, increasing the valency of the peptide conjugate should reduce the pitch of the helical assembly. A family of monovalent, divalent, and trivalent peptide conjugates [$C_x$-$(PEP_{Au})_y$, where x = 12, 14, 16, or 18 and y = 1, 2, or 3] were prepared. It was discovered that helix pitch was roughly proportional to aliphatic tail length and inversely proportional to peptide valency.[5] These results represented one of the first examples of using peptide conjugate design principles to rationally tune the structure and metrics of nanoparticle superstructures.

During the investigation into helix pitch and peptide valency it was found that some $C_{18}$-$(PEP_{Au})_2$ samples directed the formation of single-helical gold nanoparticle superstructures rather than double-helical superstructures. This unusual finding prompted rigorous characterization of the particular $C_{18}$-$(PEP_{Au})_2$ samples that led to single helix formation. Interestingly, the samples that produced single helices contained oxidized methionine residues ($C_{18}$-$(PEP_{Au}^{M\text{-}ox})_2$). Preparative methods for synthesizing the single helices were optimized and their chiroptical activity analyzed. The single helices exhibited a strong bisignate peak centered at approximately 600 nm, near the collective plasmonic extinction band (Figure 25). The chiroptical activity of the single helices were compared to other reported chiral nanoparticle assemblies. The anisotropy factor, *g*, is typically used as a benchmark value for determining the intensity of the chiroptical signal. Optimized assemblies, for which synthetic conditions were tuned to increase particle dimensions, exhibited an absolute *g*-factor up to ~0.04, which is one of the highest reported to date for comparable nanoparticle assemblies. To understand the origin of the single-helical gold nanoparticle superstructure, the morphology and assembled structure of $C_{18}$-$(PEP_{Au}^{M\text{-}ox})_2$ was studied using TEM, atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, circular dichroism (CD) spectroscopy, X-ray diffraction (XRD), and solid-state nuclear magnetic resonance spectroscopy (ssNMR). TEM and AFM revealed that $C_{18}$-$(PEP_{Au}^{M\text{-}ox})_2$ assembled into linear amyloid-like 1-D helical ribbons having structural parameters that correlated well to those of the single-helical gold nanoparticle superstructures. FTIR, CD, XRD, and ssNMR indicated the presence of cross-β and polyproline II (PPII) secondary structure. A molecular assembly model was derived that took into account all experimental observations and that supported the single-

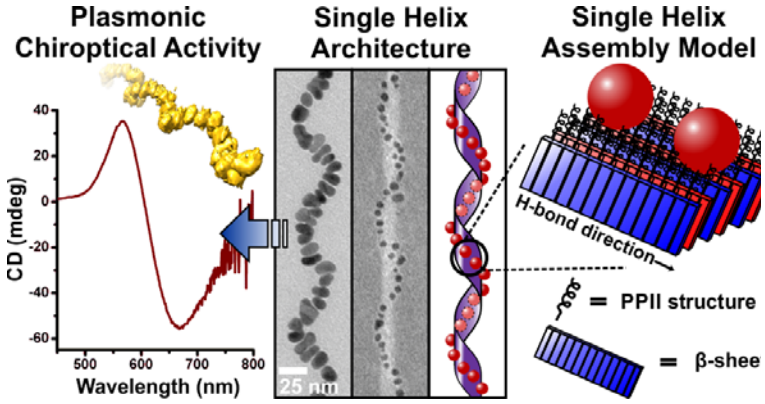


**Figure 25. Single-helical gold nanoparticle superstructures, their chiroptical response, and a structural model describing their assembly.**

helical nanoparticle assembly architecture (Figure 25).This model will serve as the basis for the design of future nanoparticle assemblies having programmable structures and properties.[30]

The **Rosi** group and **Nguyen** group initiated a collaboration to synthesize peptide-oligonucleotide chimera (POC) molecules and investigate their self-assembly behavior. It was envisaged that POCs would represent another programmable building block that could be used to direct the assembly of nanoparticles. The first studies focused on the fundamental factors (e.g. solvent, temperature, ionic strength, etc.) that influenced the assembly behavior of POCs. Two specific POCs were studied: $PO_6C$ and $PO_{18}C$. Here, P = AAAYSSGAPPMPPF and O = either a 6mer or 18mer oligonucleotide. The peptide and oligonucleotide portions were coupled together via a biphenyl bridge. The assembly of these POCs were studied. It was found that the oligonucleotide length and the ionic strength of the assembly medium were the two key factors for determining assembly morphology. $PO_{18}C$ assembled into spherical vesicular structures under most conditions; however, they assembled into fibers at high salt concentration. $PO_6C$ assembled into fibers under most conditions, but they could be coaxed into forming spherical structures at very low salt concentrations. Linear fiber formation was promoted by the formation of β-sheets between the peptide segments. This initial study was completed, and the working draft of the manuscript and supporting information included in the appendix. The basic framework for studying POCs was developed and will serve as the basis for future studies involving this new class of programmable biomolecular building block.

**WHAT'S NEXT?**

Stemming from the information learned during this MURI, more in-depth studies will be performed on dynamic and post-synthetic control of biomolecule-assembled nanoparticle structures. Further work on superlattice optical properties will be concerned with magneto-optical properties of superlattices, including the transverse magneto-optical Kerr effect, where important nonreciprocal behavior has been identified. Structural modeling will be focused on chiral assembly of peptide amphiphiles, as the MURI team has just recently discovered how to simulate ribbon and chiral helix properties. Moving forward with the characterization techniques that were developed during the MURI, mechanisms for synthesis of a wider array of nanoparticle cores will be investigated using x-ray approaches and atom probe tomography. HIRSAXS will be conducted on DNA-coated proteins in order to verify the technique and compare with ASAXS results. Simulation studies on the effect of high salt concentration during crystallization as well as additional anisotropic shapes in building blocks will be performed. Using the design rules established in this MURI, the epitaxial deposition of PAEs as a means to control material properties via lattice size and shape will be pursued as well as developing new NCT-based composites with composition and nanoscopic structure-derived properties. The toolbox of building blocks will be expanded to create unique materials and topologies. The models developed for peptide assembly will be used as a springboard for the design and preparation of new classes of helical nanoparticle assemblies with optimized chiroptical properties as POCs represent a new highly tailorable building block for the programmable construction of soft materials.

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| Andrew Lee, PhD | postdoc |
| Haixin Lin, PhD | postdoc |
| Jarad Mason, PhD | postdoc |
| Matthew Rycenga, PhD | postdoc |
| Chuan Zhang, PhD | postdoc |
| | |
| Stacey Barnaby | graduate student |
| Colin Calabrese | graduate student |
| Josh Cutler | graduate student |
| Lam-Kiu Fong | graduate student (shared with Schatz) |
| Matthew Jones | graduate student |
| Youngeun Kim | graduate student |
| Haixin Lin | graduate student |
| Andrea Luthi | graduate student |
| Robert Macfarlane | graduate student |
| Janet McMillan | graduate student |
| Kurinji Krishnamoorthy | graduate student (shared with Bedzyk) |
| Liane Moreau | graduate student (shared with Bedzyk) |
| Matt O'Brien | graduate student |
| Michael Ross | graduate student (shared with Schatz) |
| Adam Sanford | graduate student |
| Naoyuki Shimazu | graduate student |
| So Young Seo | graduate student |
| Ryan Thaner | graduate student (shared with Nguyen) |
| Mary Wang | graduate student |
| Kaylie Young | graduate student |
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| Caroline Ko, PhD | research associate |
| Tanushri Sengupta, PhD | research associate |
| Hillary Bradshaw | research technician |
| Pam Watson | project administrator |

**MACFARLANE/ATWATER**

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| Robert Macfarlane, PhD | postdoc (under Atwater) |
| Seyoon Kim | graduate student (under Atwater) |
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**SCHATZ**

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| Clotilde Lethiec, PhD | postdoc |
| Andrew Sirjoosingh, PhD | postdoc |
| Marc Bourgeois | graduate student |
| Vince Cho | graduate student |
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| Michael Ross | graduate student (shared with Mirkin) |

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| Kyle Hoffmann, PhD | postdoc |
| Kevin Kohlstedt, PhD | postdoc |
| Jaime Millan, PhD | postdoc |
| Joshua Dempster | graduate student |
| Martin Girard | graduate student |
| Ting Li | graduate student |
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| | |
|---|---|
| Jos Zwanikken, PhD | research assistant professor |

**BEDZYK**

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| Sumit Kewalramani, PhD | postdoc |
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| Liane Moreau | graduate student (shared with Mirkin) |

**NGUYEN**

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| Ibrahim Eryazici, PhD | postdoc |
| Bong-Jin Hong, PhD | postdoc |
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**ROSI**

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|---|---|
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| Chong Liu | graduate student |
| Andrea Merg | graduate student |
| Soumitra Punekar | graduate student |
| Ryan Ruenroeng | graduate student |
| Jessica Sammons | graduate student |
| Chengyi Song | graduate student |
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| Chen Zhang | graduate student |
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**PUBLICATIONS**
**MIRKIN**


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**MACFARLANE**

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13. Thaner, R.V.; Morris, W.; Lee, B.; Nguyen, S.T.; Mirkin, C.A. "High-throughput syntheses of DNA-nanoparticle superlattices", *Nanoscale* **2016**, *in preparation*

**ROSI**

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**INTERACTIONS/TRANSITIONS**

**MIRKIN**

- University of New Mexico, Chemistry Department Colloquium, Albuquerque, NM, "The Polyvalent Gold Nanoparticle Conjugate: Materials Synthesis, Biodiagnostics, and Intracellular Gene Regulation" (2011).
- American Association for Cancer Research Annual Meeting, Orlando, FL, "Ultrasensitive Approaches to the Early Detection of Cancer" (2011).

- National Institute of Standards and Technology, Gaithersburg, MD, “The Polyvalent Gold Nanoparticle Conjugate:  Material Synthesis, Biodiagnostics, and Intracellular Gene Regulation” (2011).
- ACS National Meeting, Denver, CO, “Plasmon-Mediated Syntheses of Silver Nanostructures” (2011).
- University of Texas, Austin, TX, "Spherical Nucleic Acid Nanostructures: Establishing a New Paradigm in Materials Synthesis, Molecular Synthesis, Molecular Diagnostics, and Intracellular Gene Regulation" (2011).
- University of Maryland, Baltimore, Translational Genomes to Personalized Medicine Symposium, Baltimore, MD, "Spherical and other Three-dimensional Forms of Nucleic Acids: A New Gene Regulation Platform" (2011).
- NDIA for the 25th Anniversary of the MURI Program, Washington, DC; “MURI-Funded Scientific and Technological Blockbusters from Northwestern University” (2011).
- AFOSR Program Review, National Harbor-Oxon Hill, MD, “MURI: BioProgrammable One-, Two-, and Three-Dimensional Materials” (2011).
- APS National Meeting, Boston, MA, “Nanoparticle Superlattice Engineering with DNA” (2012).
- Erik B. Young Lecture, University of Maryland, College Park, MD, “Spherical Nucleic Acid (SNA) Nanostructures: Establishing New Paradigms in Materials Synthesis, Molecular Diagnostics, and Intracellular Gene Regulation” (2012).
- ACS 243rd National Meeting, San Diego, CA, “Spherical Nucleic Acid (SNA) Nanostructures: Establishing a New Paradigm in Materials Synthesis, Molecular Diagnostics, and Intracellular Gene Regulation” (2012).
- International Workshop on Frontiers of Molecular Science, Beijing, China, “’Artificial Atoms’ Formed from Nucleic Acid-Nanoparticle Conjugates” (2012).
- 5th International Symposium on Bioanalysis, Biomedical Engineering and Nanotechnology (ISBBN), Changsha, China, “Spherical Nucleic Acid (SNA) Nanostructures: Establishing New Paradigms in Materials Synthesis, Molecular Diagnostics, and Intracellular Gene Regulation” (2012).
- ACS Fall 2012 Meeting, Philadelphia, PA, “Artificial Atoms Formed from Nucleic Acid-Nanoparticle Conjugates” (2012).
- Harvard University, Harvard-MIT P-Chem Seminar, Cambridge, MA, “Programmable Atom Equivalents” (2012).
- Argonne National Laboratory, Joint NSRC Workshop on Nanoparticle Science, Lemont, IL, “'Artificial Atoms' Formed from Nucleic Acid-Nanoparticle Conjugates” (2012).
- Natural Materials, Systems & Extremophiles Program Review, Washington, DC, “MURI Bioprogrammable 1, 2, 3D Materials” (2013).
- AAAS Annual Meeting, Boston, MA, "Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New Periodic Table" (2013).
- MRS Spring Meeting, San Francisco, CA, "Programmable Aton Equivalents" (2013).
- ACS National Meeting, New Orleans, LA, "Programmable Atom Equivalents" (2013).

- GRC Conference, Les Diablerets, Switzerland, "Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New Periodic Table" (2013).
- Cambridge University, Lord Lewis Lectureship, Cambridge, UK, "Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New Periodic Table" (2013).
- New York University, Programmable Self-Assembly of Matter Conference, New York, NY, "Ternary Nanoparticle Superlattices through Topotactic Intercalation" (2013).
- OSD MURI Program Review, Arlington, VA, "BioProgrammable One-, Two-, and Three-Dimensional Materials" (2013).
- Gordon Research Conference, South Hadley, MA, "'Artificial Atom' Formed from Nucleic Acid-Nanoparticle Conjugates" (2013).
- ACS National Meeting, Indianapolis, IN, "Ternary Nanoparticle Superlattices through Topotactic Intercalation" (2013).
- University of Portland, Linus Pauling Medal Symposium, Portland, OR, "Programmable Atom Equivalents from Spherical Nucleic Acid (SNA) Nanoparticle Conjugates: Defining a New 'Table of Elements'" (2013).
- Princeton University, Crocco Colloquium, Princeton, NJ, "Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New 'Table of Elements'" (2013).
- De Long Annual Natural Materials and Systems Program Review, Fort Walton Beach, FL, "MURI: BioProgrammable One-, Two-, and Three-Dimensional Materials" (2013).
- 12th US-Japan Symposium on Drug Delivery Systems, Lahaina, Maui, Hawaii, "Spherical Nucleic Acid (SNA) Nanostructures: Establishing a New Paradigm in Molecular Diagnostics and Intracellular Gene Regulation" (2013).
- Workshop on Advanced Materials, Ras al Khaimah, Qatar, "Spherical Nucleic Acid (SNA) Nanostructures: Establishing a New Paradigm in Molecular Diagnostics and Intracellular Gene Regulation" (2014).
- International Workshop on Advanced Materials, Dubai, UAE, "Spherical Nucleic Acids as Programmable Atom Equivalents: Constructing a New 'Table of Elements'" (2014).
- PITTCON, Chicago, IL, "Spherical Nucleic Acids (SNAs): Novel Therapeutic Agents for Cancer Treatment" (2014).
- PITTCON, Chicago, IL, "A Chemist's Approach to Nanofabricaton: Towards a 'Desktop Fab'" (2014).
- American Chemical Society, Dallas, TX, "Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New 'Table of Elements'" (2014.)
- American Chemical Society, Dallas, TX, "'Nano-flares' for the Analysis of Circulating Cancer Cells" (2014).
- American Chemical Society, Dallas, TX, "Spherical Nucleic Acid (SNA) Nanostructures: Establishing a New Paradigm in Molecular Diagnostics and Intracellular Gene Regulations" (2014).
- American Association for the Advancement of Science, Chicago, IL, "Convergence Science: A Revolution for Health Solutions" (2014).

- American Association for Cancer Research, San Diego, CA, “Spherical Nucleic Acids for the Treatment of Glioblastoma Multiforme” (2014).
- In Vivo Nanoplatforms Review, San Diego, CA, “Spherical Nucleic Acids for In Vivo Therapeutics” (2014).
- California Institute of Technology, Pasadena, CA, “Spherical Nucleic Acid (SNA) Nanostructures: Establishing a New Paradigm in Molecular Diagnostics and Intracellular Gene Regulation” (2014).
- Nanjing University of Technology, Nanjing, China, “Spherical Nucleic Acids: A New Paradigm in Intracellular Gene Regulation and Molecular Diagnostics” (2014).
- Nanjing University of Technology, Nanjing, China, “Cantilever-free Molecular Printing: Toward a ‘Desktop Fab’” (2014).
- The Sixth International Symposium on Bioanalysis, Biomedical Engineering, and Nanotechnology, Hunan University, Changsha, China, “Intracellular Fate of Spherical Nucleic Acid Nanoparticle Conjugates” (2014).
- The Tenth Nanoscience and Nanotechnology Conference, Istanbul, Turkey, “Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New ‘Table of Elements’” (2014).
- Gordon Research Conferences Bioanalytical Sensors, Salve Regina University, Providence, Rhode Island, “‘Nano-flares’ for the Analysis of Circulating Cancer Cells” (2014).
- The Twelfth International Conference on Nanostructured Materials, Moscow, Russia, “Spherical Nucleic Acid (SNA) Nanostructures as Intracellular Probes and Gene Regulation Agents” (2014).
- NBIT Program Review and Nanoscience Technical Exchange, University of California, Berkeley, CA, “Plasmonic Optoelectronic Interactions” (2014).
- 2014 Annual Beckman Symposium, Irvine, CA, “The Nature of the DNA Bond” (2014).
- 248$^{th}$ ACS National Meeting, San Francisco, CA, “Materials by Design from Programmable Atom Equivalents (PAEs)” (2014).
- 248$^{th}$ ACS National Meeting, San Francisco, CA, “Coaxial Lithography” (2014).
- 248$^{th}$ ACS National Meeting, San Francisco, CA, “Spherical Nucleic Acid (SNA) Nanostructures: Enabling Tools for Biomedical Applications” (2014).
- 248$^{th}$ ACS National Meeting, San Francisco, CA, “Nature and Implications of Near-Perfect Nanoparticle Seeds” (2014).
- ISACS Meeting on Nanoscience, San Diego, CA, “Spherical Nucleic Acids as Programmable Atom Equivalents: Constructing a New ‘Table of Elements’” (2014).
- Fermilab Arts & Lecture Series, Batavia, IL, “Nanotechnology: Learning to Think Big in a Field Focused on the Small” (2014).
- NCI Alliance for Nanotechnology in Cancer Annual Investigator’s Meeting, Rockville, MD, “Nanomaterials for Cancer Diagnostics and Therapeutics” (2014).
- SmithGroupJJR Distinguished Lecture, Beckman Institute for Advanced Science and Technology, UIUC, Urbana, IL, “The Nature of the DNA Bond” (2014).
- Multidisciplinary Chemistry Without Borders, Porto Alegre, Brazil, “Cantilever-Free Scanning Probe Lithography: Towards a ‘Desktop Fab’” (2014).

- Multidisciplinary Chemistry Without Borders, Porto Alegre, Brazil, “Revolutionizing the Field of Medicine through Advances in Nanotechnology” (2014).
- American Association of Pharmaceutical Scientists Annual Meeting and Exposition, San Diego, CA, “Spherical Nucleic Acid (SNA) Nanostructures for Advanced Wound Healing Applications” (2014).
- UCSD Department of Bioengineering, Skalak Memorial Lecture, San Diego, CA, “Spherical Nucleic Acid (SNA) Nanostructures as Intracellular Probes and Gene Regulation Agents” (2014).
- PITTCON, New Orleans, LA, “Liposomal SNAs: A New Approach to Gene Regulation Therapy” (2015)
- ACS Spring 2015 National Meeting, Denver, CO, “Nanotechnology: Delivering the Promise - R&D” (2015).
- ACS Spring 2015 National Meeting, Denver, CO, “Programmable Atom Equivalents from Nucleic-Acid Modified Nanostructures: Constructing a New ‘Table of Elements’” (2015).
- MRS 2015 Spring Conference, San Francisco, CA, “Liposomal Spherical Nucleic Acids: A New Approach to Immuno-Modulatory and Regulation Therapies” (2015).
- MRS 2015 Spring Conference, San Francisco, CA, “The Nature and Implications of Near-Perfect Nanoparticle Seeds” (2015).
- MRS 2015 Spring Conference, San Francisco, CA, “The Design Principals for Colloidal Crystals made from Proteins Modified with Nucleic Acids” (2015).
- Workshop in NanoScience and NanoEngineering, Duke University, Durham, NC, “Programmable Atom Equivalents from Nucleic-Acid Modified Nanostructures: Forging a New ‘Table of Elements’” (2015).
- National Security Science and Engineering Faculty Fellowship 2014 Class Orientation, Arlington, VA, “Functional Crystals through Encodable Hard and Soft Matter” (2015).
- Phi Lambda Upsilon-Rho Chapter Award Lecture, University of Nebraska – Lincoln, Lincoln, NE, “The Nature of the DNA Bond” (2015).
- Department of Chemistry Inorganic Harvard/MIT Seminar Series, MIT, Cambridge, MA, “Spherical Nucleic Acids as Programmable Atom Equivalents: Constructing a New ‘Table of Elements’” (2015).
- UNC Center for Nanotechnology in Drug Delivery Eshelman School of Pharmacy Distinguished Speaker Seminar, Chapel Hill, NC, “Liposomal Spherical Nucleic Acids: A New Approach to Immunomodulatory Therapies” (2015).
- CIC biomaGUNE Seminar, San Sebastian, Spain; “Programmable Atom Equivalents from Nucleic Acid-Modified Nanoparticle Constructs” (2015).
- ICBN Workshop: Revolutionizing Biology and Medicine with Advances in Nanotechnology, Hunan University, Changsha, China, “Liposomal Spherical Nucleic Acids (SNAs): New and Potent Agents for Immunomodulatory Therapies” (2015).
- Shanghai Tech Advances in Research (STAR) Symposium, Shanghai, China, “Liposomal Spherical Nucleic Acids: A New Approach to Immunomodulatory Therapies” (2015).
- GRC Nucleosides, Nucleotides & Oligonucleotides, Salve Regina University, Newport, RI, “Programmable Materials and the Nature of the DNA Bond” (2015).

- IARPA Bio Intelligence Chips Program PI Meeting, Livermore, CA, “Biodiagnostic Approaches to Human Profiling Through Nanomaterial Indicators” (2015).
- Karle Symposium, University of Michigan, Ann Arbor, MI, ““Programmable Materials and the Nature of the DNA Bond” (2015).
- Frontiers Seminar, Case Western University, Cleveland, OH, “Programmable Materials and The Nature of the DNA Bond” (2015).
- President’s Science Symposium, Bowdoin College, Brunswick, ME, “Nanotechnology: A Small World with Big Potential” (2015).
- Department of NanoEngineering Seminar Series, UCSD, San Diego, CA, “Liposomal Spherical Nucleic Acids: A New Approach to Immunomodulatory Therapies (2015).
- Illumina Scientific Advisory Board Meeting, San Diego, CA, “The Convergence of Nanoscience with Biology and Medicine” (2015).
- Peking University, Beijing, China, “Nanocombinatorics Through Scanning-Probed Based Chemistry and Biology” (2015).
- MRS Fall Meeting, Boston, MA, “Programmable Materials and the Nature of the DNA Bond” (2015).
- MRS Fall Meeting, Boston, MA, “Advanced RNA Analysis in Live Cells via Stickyflare Nanoconjugates” (2015).
- MRS Fall Meeting, Boston, MA, “Liposomal SNAs as Immunomodulatory Agents for Cancer Vaccines” (2015).
- AFOSR Natural Materials and Systems Program Review, Destin, FL, “MURI: Nanostructured Interfaces and Patterning Tools for Probing Bioinspired Materials and Systems” (2015).
- 13th US-Japan Symposium on Drug Delivery Systems, Maui, HI, “Liposomal SNAs as Powerful Immunomodulatory Agents” (2015).
- DOE Energy Frontier Research Centers Center for Bio-Inspired Energy Science Mid-Term Review, Gaithersburg, MD, “Pluripotent Nanoparticles: Reconfigurable Programmable Atom Equivalents” (2016).
- Air Force Research Laboratory Human Performance Seminar, Dayton, OH, “Profiling State of Health with Biomarkers Identified Based Upon Ultrahigh Sensitivity, Highly Multiplexed Assays” (2016).
- Pittcon Conference, Atlanta, GA, “Tracking the Amount and Location of RNA in Single Cells” (2016).
- Pittcon Conference, Atlanta, GA, “Liposomal SNAs: A New Approach to Immunomodulatory Therapy” (2016).
- ACS Spring 2016 Conference, San Diego, CA, “Pluripotent nanoparticles with programmable and responsive DNA bonds” (2016).
- ACS Spring 2016 Conference, San Diego, CA, “Liposomal spherical nucleic acids: Nanostructures enabling the potential of therapeutic nucleic acids” (2016).
- ACS Spring 2016 Conference, San Diego, CA, “Nanocombinatorix via scanning probe block copolymer lithography” (2016).

- Baylor University Medical Center at Dallas Internal Medicine Grand Rounds, Dallas, TX, “Realizing the Promise of Nanomedicine” (2016).
- Baylor University Medical Center at Dallas Internal Medicine, Dallas, TX, “Spherical Nucleic Acids: A New Platform in Immunotherapy” (2016).
- NSSEFF Spring Meeting, Adelphi, MD, “Functional Crystals through Encodable Hard and Soft Matter” (2016).
- Royal Society of Chemistry Centenary Prize Lecture Series, Glasgow University, Glasgow, Scotland, “Programmable Atom Equivalents and the Nature of the DNA Bond” (2016).
- ICBN Workshop: Revolutionizing Biology and Medicine with Advances in Nanotechnology, Hunan University, Changsha, China; “Liposomal Spherical Nucleic Acids (SNAs): New and Potent Agents for Immunomodulatory Therapies” (2015).
- Royal Society of Chemistry Centenary Prize Lecture Series, University of Oxford, Oxford, England, “Programmable Atom Equivalents and the Nature of the DNA Bond” (2016).
- Royal Society of Chemistry Centenary Prize Lecture Series, Imperial College of London, London, England, “Programmable Atom Equivalents and the Nature of the DNA Bond” (2016).
- Young Investigator Network Lecture Series, Karlsruhe Institute of Technology, Karlsruhe, Germany, “The Convergence of Nanoscience and Nanomedicine: New Approaches for Studying, Tracking, and Treating Disease” (2016).
- Aerospace Medical Association 87th Annual Scientific Meeting, Atlantic City, NJ, “Biomarker Detection Using Spherical Nucleic Acids” (2016).
- Wuxi University, China, "Programmable Materials and the Nature of the DNA Bond" (2016).
- Fudan Materials Beyond Symposium, Fudan University, China, “Colloidal Crystallization with DNA: Unlocking the Source Code for Materials by Design” (2016).
- The 7th International Symposium on Bioanalysis, Biomedical Engineering and Nanotechnology, Hunan University, Changsha, China, “Nanostructures for Tracking RNA in Live Cells with Single Cell Resolution” (2016).
- Young Giants of Nanoscience 2016, The Hong Kong Polytechnic University, Hong Kong, “Unlocking the Materials Genome Through Nanocombinatorix” (2016).
- Center of Excellence for Advanced Bioprogrammable Nanomaterials Annual Review, AFRL, Dayton, OH, “Screening Nanotube Catalysts through Scanning Probe Block Copolymer Lithography” (2016).
- Center of Excellence for Advanced Bioprogrammable Nanomaterials Annual Review, AFRL, Dayton, OH, “Rapid Quantification of Salivary Cortisol through Nanoflares” (2016).

**MACFARLANE**

- The use of Argonne National Laboratory’s Advanced Photon Source enabled characterization of superlattice materials (synchrotron small angle X-ray scattering with Dr. Byeongdu Lee)
- Macfarlane gave invited presentations at:
  March 2014, “Nanoparticle Superlattice Engineering with DNA”
  NYU Soft Matter Institute, NY

September 2014, “Programmable Self-Assembly with Particles and Polymers”
UCSD Nanoengineering Department, CA
June 2016, “DNA-Directed Assembly of ‘Programmable Atom Equivalents’”
Materials Design and Processing from Nano to Mesoscale, Cornell, NY
July 2016, “DNA-Directed Assembly of ‘Programmable Atom Equivalents’”
Micro- and Nanotechnologies for Medicine Workshop, MIT, MA
September 2016, “DNA-Directed Assembly of ‘Programmable Atom Equivalents’”
University of Nebraska Lincoln Nanotechnology Seminar Series

- Santos was awarded the National Science Foundation’s Graduate Research Fellowship; Gabrys was awarded Honorable Mention

**SCHATZ**

- Schatz received an Honorary Doctorate, Clarkson University – 2012
- Schatz received the S F Boys-A Rahman Award of the Royal Society of Chemistry – 2013
- Schatz was named Fellow of the Royal Society of Chemistry (FRSC) – 2013
- Schatz received the Hirschfelder Prize, University of Wisconsin – 2014
- Schatz was named a 2014 Highly Cited Researcher by Thompson-Reuters based on 2002-2012 – 2014
- Schatz received the Mulliken Medal, University of Chicago – 2014
- Schatz was named John Stauffer Lecturer, USC – 2015
- Schatz was the Edgar Fahs Smith Lecturer, University of Pennsylvania – 2016
- Schatz received the Irving Langmuir Award in Chemical Physics, American Chemical Society – 2016
- Schatz was the Condon Lecturer, University of Colorado, Boulder – 2016
- Schatz was a Distinguished Lecturer, Materials Science and Engineering, RPI – 2016
- Schatz gave a talk at the Inaugural Symposium on Computational Science, Temple University, Oct. 18, 2013, entitled “Coupling Self-Assembly to Plasmons”
- Schatz gave a talk at University of Bristol, March 24, 2014, entitled “New plasmonic materials and optical applications: theory drives experiment”
- Schatz gave a talk at University of Manchester, March 25, 2014 entitled “New plasmonic materials and optical applications: theory drives experiment”
- Schatz gave a talk at University of York, March 26, 2014, at the RSC Symposium, entitled “New plasmonic materials and optical applications: theory drives experiment”
- Schatz gave two talks at the Korean Chemical Society Meeting, Seoul Korea April 17, 2014
    - Plenary Talk: Plasmon-molecule interactions
    - Keynote Talk: New directions in the assembly of functional materials
- Schatz gave a talk at the 2014 Yonsei International Symposium on Nano-Bio Molecular Assembly, Seoul Korea, April 18-19, 2014 entitled “New Directions in the Assembly of Functional Materials”
- Schatz gave a talk at Pusan University, Pusan Korea, April 25, 2014, entitled “New directions in the assembly of functional materials”
- Schatz gave a talk at Leibniz Institute, Jena, Germany, August 6, 2014 entitled “Plasmonic Arrays”
- Schatz gave a talk at the University of Illinois, Urbana IL Feb. 19, 2015 entitled “Silver and Gold Nanoparticles: New Directions for Theory”

- Schatz gave an invited talk at ACS National Meeting, Denver, CO March 22-24, 2015 entitled: “Plasmon/exciton and plasmon/photonic mode interaction”
- Schatz gave a talk at MRS Spring Meeting, San Francisco, CA April 6-10, 2015 entitled: “Plasmonic Arrays”
- Schatz gave a talk at the Center for Nanomaterials (CNM) Workshop on Nanophotonics, Argonne National Laboratory, May 12, 2015 entitled “Plasmonic Arrays”
- Schatz gave a talk at the International Congress on Quantum Chemistry, Tsinghua University, Beijing, China, June 8-12, 2015 entitled “Plasmonic Arrays” (Plenary Lecturer)
- Schatz gave a talk at MU3C (Midwest Universities Computational Chemistry Conference), Evanston IL July 23, 2015 entitled “Connecting small and large length scales for metal nanoparticle optical properties”
- Schatz gave a talk entitled “New directions in plasmonic materials and SERS applications” at the SPP6 Meeting, Ottawa, Canada May 29-31, 2013
- Schatz gave a talk entitled “Discovering Plasmonic Materials” at the “Materials Genome Initiative Grand Challenges Summit”, NIST, Rockville MD, June 25, 2013
- Schatz gave a talk entitled “New directions in plasmonics: SERS and nanoparticle superlattice crystals” at the Piers 2013 Conference, Stockholm Sweden, August 13, 2013
- Schatz gave a talk entitled “Modeling Active Plasmonic Response” at the SPIE conference, San Diego Aug. 25-27, 2013

**OLVERA**

- Olvera gave a plenary lecture on self-assembly and supramolecular chemistry, Gordon Research Conference, May 5-10$^{th}$, 2013, Les Diablerets, Switzerland
- M. Olvera de la Cruz, J. W. Zwanikken, P. Guo, R. J. Macfarlane, and C. A. Mirkin, “Grafting density effect on ionic screening around functionalized Nanoparticles”, 241st ACS National Meeting & Exposition - March 27-31, 2011, Anaheim, California.
- T. Li, R. Sknepnek, R.J. Macfarlane, C.A. Mirkin and M. Olvera de la Cruz, “Modeling of DNA-directed colloidal self-assembly and crystallization”, American Physical Society March Meeting, Boston, MA, February 27- March 2, 2012.
- M. Olvera de la Cruz, “The stability of polyvalent nanoparticles and effective interactions in molecular electrolytes” XXI International Materials Research Congress (IMRC), August 13-17, 2012, Cancun, Mexico.
- S. Kewalramani, C-Y. Leung, J. Zwanikken, R. Macfarlane, M. Olvera de la Cruz, C. Mirkin, and M. Bedzyk, “Determination of counterion distribution around DNA coated nanoparticles (DNA-AuNP) by small angle X-ray scattering (SAXS),” American Physical Society March Meeting, Baltimore, MD, March 18-22, 2013.
- T.I.N.G. Li, R. Sknepnek, and M. Olvera de la Cruz, “Hybridization dynamics to DNA guided crystallization,” American Physical Society March Meeting, Baltimore, MD, March 18-22, 2013.
- K.L. Kohlstedt, M. Olvera de la Cruz, and G.C. Schatz, “Controlling orientational order of multivalent prisms in superlattice assemblies,” American Physical Society March Meeting, Baltimore, MD, March 18-22, 2013.
- M. Olvera de la Cruz, “Electrostatics in Spherical Nucleic Acid-Au Nanoparticle Assemblies" Programmable Self-Assembly of Matter workshop (June 30-July 2, NYC), 2013.

- M. Olvera de la Cruz, “Spherical Nucleic Acid-Au Nanoparticle Assemblies”, Materials Research Society Fall Meeting, Dec 1-6, 2013, Boston, MA.
- M. Olvera de la Cruz, “DNA-Functionalized Nanoparticle Assembly and Crystallization,” Dept. of Materials Science and Engineering, University of California, Berkeley, February 11, 2014.
- T. Li, E. Auyeung, C.A. Mirkin and M. Olvera de la Cruz, “Multi-scale modeling for the self-assembly of DNA-functionalized nanoparticle into superlattice and Wulff polyhedra”, APS March meeting, Denver, CO, March 3-7, 2014.
- C. Mirkin, R.J. Macfarlane, E. Auyeung, M. Olvera de la Cruz, “Nucleic acid-modified nanostructures as programmable atom equivalents: Forging a new “Table of Elements”, ACS National Meeting, Dallas, Texas, March 16-20, 2014.
- M. Olvera de la Cruz, “DNA-Functionalized Nanoparticle Assembly and Crystallization,” Dept. of Chemical Engineering, University of Texas at Austin, Austin TX, March 27, 2014.
- T. Li, E. Auyeung, C.A. Mirkin, M. Olvera de la Cruz, “Self-Assembly and Crystallization of DNA-Functionalized Nanoparticle into Wulff Polyhedra”, MRS Spring Meeting, San Francisco, California, April 21-25, 2014.
- M. Olvera de la Cruz, “DNA-Functionalized Nanoparticle Assembly and Crystallization,” Dept. of Materials Science and Eng. Colloquium, University of Illinois Urbana, November 17, 2014.
- Ting Li, Monica Olvera de la Cruz, “DNA-programmable Nanoparticle Self-Assembly and Crystallization via Multi-Scale Modelling & Simulation” APS Spring Meeting, San Antonio, TX, March 2-6, 2015.
- Sumit Kewalramani, Liane Moreau, Guillermo Guerrero-Garcia, Monica Olvera de la Cruz and Michael Bedzyk, “Counterion-mediated assembly of spherical nucleic acid-Au nanoparticle conjugates (SNA-AuNPs)” APS Spring Meeting, San Antonio, TX, March 2-6, 2015.
- M. Olvera de la Cruz “DNA-functionalized Nanoparticle Assembly and Crystallization” SIAM Conference on Computational Science and Engineering, Salt Lake City, UT, March 14-18, 2015.
- M. Olvera de la Cruz “DNA-functionalized Nanoparticle Assembly” NU Computational Research Day, April 14, 2015.
- M. Olvera de la Cruz “DNA-functionalized Nanoparticle Assembly” Rutgers University, Jamestown, MI, April 1, 2015
- M. Olvera de la Cruz “DNA-functionalized nanoparticle assembly” ACS National Meeting, Denver, CO, March 22-27, 2015.
- M. Olvera de la Cruz, “DNA-functionalized nanoparticle assembly and crystallization” Frontiers of Polymer Science, Chinese Academy of Sciences, China, Aug 8-10, 2015.
- M. Olvera de la Cruz, “DNA-functionalized Nanoparticle Assembly” Rutgers University, Sept 22, 2015
- M. Olvera de la Cruz, “DNA-functionalized nanoparticle assembly” Chemical Engineering Colloquium, Penn State University, Oct 7, 2015
- Monica Olvera de la Cruz "Assembly of anisotropic functionalized particles" Physics Colloquium, University of California, Santa Cruz, CA, March 3, 2016
- M. Olvera de la Cruz, “DNA-functionalized nanoparticle assembly” MRSEC-UC Santa Barbara, Santa Barbara, CA, February 25, 2016

- Monica Olvera de la Cruz "DNA-Functionalized Nanoparticle Assembly" Materials Science Colloquium, Caltech, CA, February 24, 2016
- Monica Olvera de la Cruz ""DNA-Functionalized Nanoparticle Assembly"" Materials Science Seminar Series, U. C. Berkeley, Berkeley, CA, February 18, 2016
- M. Olvera de la Cruz, "DNA-functionalized anisotropic particle assembly" ACS National Meeting, San Diego, CA, March 13-17, 2016
- J. Millan, M. Girard, J. Brodin, M. O'Brien, C. Mirkin, M. Olvera de la Cruz, "Modeling of DNA-Mediated Self-Assembly from Anisotropic Nanoparticles: A Molecular Dynamics Study" APS Meeting, Baltimore, MD, March 14-18, 2016
- S. Kewalramani, M. Bedzyk, L. Moreau, J. Zwanikken, C. Mirkin, M. Olvera de la Cruz, "Electrolyte-Mediated Assembly of Charged Nanoparticles" APS Meeting, Baltimore, MD, March 14-18, 2016
- Monica Olvera de la Cruz, "The Shape of Single Soft Crystals" Computations in Science Seminar, University of Chicago, IL, April 13, 2016
- Monica Olvera de la Cruz, "Assembly of anisotropic functionalized particles" 28th International Conference on Science and Technology of Complex Fluids, Physic Department, Universidad Nacional Autonoma de San Luis Potosi, Mexico, June 20-24, 2016.
- Ting Li awarded Ryan Fellowship 2012-2014
- Jaime Millan awarded an International Institute for Nanotechnology Fellowship 2015-2017
- Kyle Hoffmann awarded an International Institute for Nanotechnology Fellowship 2015-2017.

**BEDZYK**

- Collected x-ray data at the Advanced Photon Source at Argonne National Laboratory, working with staff from Sector 5: DND-CAT (Steven Weigand and Qing Ma)
- Michael Bedzyk was inducted as a fellow of American Association for the Advancement of Science (2013)
- Liane Moreau awarded National Defense Science and Engineering Graduate (NDSEG) Fellowship (2013)
- Sumit Kewalramani was awarded IIN Outstanding Researcher Award (2014)
- Liane Moreau awarded NU Fellowship in Leadership (2015)
- Liane Moreau was awarded a best student poster award at the APS User's Meeting (2016)
- Sumit Kewalramani presented at the American Physical Society March Meeting, Baltimore, U.S.A., "Determination of Counterion Distribution around DNA-Coated Nanoparticles" (2013).
- Sumit Kewalramani presented at the Indo-U.S. Scientific Workshop, Jawaharlal Nehru Center for Advanced Scientific Research, Bengaluru, India, "In Situ X-ray Scattering Studies on Soft Matter Systems in Aqueous Solutions" (2013).
- Sumit Kewalramani presented at the Programmable Self-Assembly of Matter Conference, New York University, New York, U.S.A, "SAXS Analysis of Counterion Distribution Surrounding Spherical Nucleic Acid- Au Conjugates" (2013).
- Liane Moreau presented at the Programmable Self-Assembly of Matter Conference, New York University, New York, U.S.A, "X-ray Scattering and Absorption Studies of DNA-Au Nanoparticle Functionalization and Assembly" (2013).

- Michael Bedzyk presented at the *NU-JNCASR workshop*, Bangalore, India, "Looking for Atoms at Complex Interfaces" (2013).
- Michael Bedzyk presented at Penn State University, Materials Science Colloquium, State College, U.S.A., "Looking for Atoms at Complex Interfaces" (2013).
- Michael Bedzyk presented at Shanghai Jiao Tong University, *Materials Science Colloquium*, Shanghai, China, "Looking for Atoms at Complex Interfaces" (2013).
- Michael Bedzyk presented at the Shanghai Synchrotron Radiation Facility Seminar, Shanghai, China, "Looking for Atoms at Complex Interfaces" (2013).
- Michael Bedzyk presented at Michigan State University, Materials Science Colloquium, Lansing, U.S.A., "Looking for Atoms at Complex Interfaces" (2014).
- Liane Moreau presented at the APS User Science Seminar, Advanced Photon Source, Argonne, U.S.A., "The Role of Ag in the Underpotential Deposition-Based Synthesis of Au Nanorods" (2014).
- Michael Bedzyk presented at the University of Minnesota, Materials Science Colloquium, Minneapolis, U.S.A., "Looking for Atoms at Complex Interfaces" (2014).
- Michael Bedzyk presented at the University of Illinois at Urbana-Champaign, Materials Science Colloquium, Champaign, U.S.A., "Looking for Atoms at Complex Interfaces" (2014).
- Michael Bedzyk presented at the Northwestern University, ANSER Seminar, Evanston, U.S.A., "Looking for Atoms at Complex Interfaces" (2014).
- Michael Bedzyk presented at Rice University, Materials Science Colloquium, Houston, U.S.A., "Looking for Atoms at Complex Interfaces" (2014).
- Sumit Kewalramani presented at the American Physical Society March Meeting, San Antonio, U.S.A., "Counterion Mediated Assembly of Spherical Nucleic Acid-Au Nanoparticle Conjugates" (2015).
- Michael Bedzyk presented at the NIMS Conference, Tsukuba, Japan, "Looking for Atoms at Complex Interfaces" (2015).
- Michael Bedzyk presented at the University of Maryland, Materials Science Colloquium, College Park, U.S.A., "Looking for Atoms at Complex Interfaces" (2015).
- Michael Bedzyk presented at Northwestern University, UNICAT Symposium, Evanston, U.S.A., "Looking for Atoms at Complex Interfaces" (2015).
- Michael Bedzyk presented at Georgia Tech, Materials Science Colloquium, Atlanta, U.S.A., "Looking for Atoms at Complex Interfaces" (2015).
- Sumit Kewalramani presented at the American Physical Society March Meeting, Baltimore, U.S.A., "Electrolyte-Mediated Assembly of Charged Nanoparticles" (2016).
- Kurinji Krishnamoorthy presented at the American Physical Society March Meeting, Baltimore, U.S.A., "Counterion Distribution Around Protein-SNAs Probed by Small Angle X-ray Scattering" (2016).
- Sumit Kewalramani presented at the Advanced Photon Source User Meeting, Argonne, U.S.A, "Electrolyte-Mediated Assembly of Highly Charged Nanoparticles" (2016).
- Liane Moreau presented at the Advanced Photon Source User Meeting, Argonne, U.S.A, "Exploring the Mechanism behind Galvanic Exchange in Nanoparticles" (2016).
- Michael Bedzyk presented at UC Berkeley, Materials Science Colloquium, Berkeley, U.S.A., "Looking for Atoms at Complex Interfaces" (2016).
- Michael Bedzyk presented at Lawrence Berkeley National Lab, Advanced Light Source Seminar, Berkeley, U.S.A., "Looking for Atoms at Complex Interfaces" (2016).

- Michael Bedzyk presented at Tel Aviv University, Materials Science Colloquium, Tel Aviv, Israel, “Looking for Atoms at Complex Interfaces” (2016).
- Michael Bedzyk presented at the Denver X-ray Conference, Chicago, U.S.A., “Combined Use of In-House and Synchrotron X-ray Facilities for Teaching and Research” (2016).

**NGUYEN**

- Dr. Byeongdu Lee of Argonne National Laboratory’s Advanced Photon Source helped us extensively in the characterization of superlattice materials using synchrotron small angle X-ray scattering.
- Andre Merg (graduate student in Rosi group) and Ryan Thaner (graduate student in Mirkin/Nguyen group) collaborated on synthesizing oligonucleotide-peptide conjugate molecules
- Eryazici gave a talk at Dow Chemical Co., Midland, MI; “Emerging design principles for DNA supramolecular assemblies with cooperative melting properties” (2011)
- Hong was awarded Best Poster Award for a postdoc at CMIDD's Seventeenth Annual Drug Discovery Symposium (2012)
- Thaner was awarded Best Organic TA (Department of Chemistry, Northwestern University) (2012)
- Chipre was awarded NIH Biophysics training fellowship (Northwestern University) (2012)
- Thaner was awarded National Science Foundation Graduate Research Fellowship (2013)
- Eryazici gave a talk at Dow Chemical Co., Midland, MI; “Nanostructures based on small molecule DNA-hybrids and their emerging design principles” (2013)
- Eryazici gave a talk at PPG Industries, Pittsburgh, PA; “Nanostructures based on small molecule DNA-hybrids and their emerging design principles” (2013)
- Hong was awarded KEMIN Travel Award for 2014 ACS Spring Meeting (2013)
- Hong was awarded Munchin Travel Fellowship for 2014 ACS Spring Meeting (2013)
- Hong gave a talk at the 247th ACS National Meeting & Exposition, Boston, MA; “Acid-Degradable Polymer-caged Lipoplex (PCL) Platform for siRNA Delivery: Facile Cellular Triggered Release of siRNA” (2014)
- Thaner gave a talk at the Gordon Research Seminar, Self-Assembly and Supramolecular Chemistry, Lucca, Italy; “The Importance of DNA “Bonds” in Nanoparticle Crystallization” (2015)
- Hong gave a talk at Pacific Biosciences, Inc., Menlo Park, CA; “Spacing-Controlled Surface Modification and Self-Assembly for Highly Efficient DNA Sensing and Gene Delivery” (2015)
- Hong gave a talk at Alios BioPharma, Inc., South San Francisco, CA; “Organic Nanoparticles for Gene Therapy” (2015)
- Hong gave a talk at DGIST, Daegu, South Korea; “Organic Nanoparticles for Chemotherapy and Gene Therapy” (2015)
- Nguyen gave a talk at School of Pharmaceutical Science and Technology (SPST), Tianjin University, Tianjin, China; “Organic-DNA hybrids for the assembling of DNA-linked macrostructures” (2015)
- Nguyen gave a talk at the Tsinghua Symposium on Frontiers of Supramolecular Science at Tsinghua University, Beijing, China; “DNA-directed assembly of supramolecular structures and nanoparticles” (2015)

- Nguyen gave a talk at the 25th AACGE Western Section Conference on Crystal Growth & Epitaxy, South Lake Tahoe, CA; "DNA-directed assembly of supramolecular structures and nanoparticles" (2016).
- Nguyen was named by Thomson Reuters as a Highly Cited Researcher (2014, 2015)
- Thaner was awarded International Travel Grant from Phi Lambda Upsilon-Alpha Gamma Chapter (2015)
- Nguyen was named List of Most Cited Researchers in Materials Science and Engineering by Elsevier Scopus Data (2016)
- Nguyen was named Thomson Reuters Highly Cited Researcher (2015)
- Nguyen was awarded Karl Rosengren Faculty Mentoring Award (2016)
- Nguyen was awarded UCC Distinguished Teaching Award (2015)
- Nguyen was awarded ASG Faculty Honor Roll Award for Distinguished Teaching (2015)
- Nguyen was awarded WCAS Award for Excellence in Mentoring Undergraduate Research (2016)
- Beard was awarded J. C., Nanomaterials Undergraduate Research in Germany (NanoRinG) at the Technical University of Munich (2016)

**ROSI**

*Awards/Recognition/Transitions:*

- Nathaniel Rosi promoted to Associate Professor with tenure (2012)
- Nathaniel Rosi named Kavli Fellow (2012)
- Chong Liu received Graduate Excellence Fellowship (2013)
- Dr. Chengyi Song defends his dissertation, accepts faculty position at Shanghai Jiao-Tong University (2013)
- Nathaniel Rosi awarded Chancellor's Distinguished Research Award (2014)
- Nathaniel Rosi listed as a 'Highly Cited Chemist' 2002-2012 (2014)
- Dr. Chen Zhang defends his dissertation, accepts postdoc position at the University of Missouri (2015)
- Soumitra Punekar received Graduate Excellence Fellowship (2015-2016)
- Nathaniel Rosi invited as 'Visiting Alumni Scholar', Grinnell College (2016)
- Nathaniel Rosi listed as a 'Highly Cited Chemist' 2004-2014 (2016)

*Personnel Exchanges:*

- Andre Merg (Rosi Lab) visited AFRL for 5 days in Spring 2014 to conduct studies with Joseph Slocik and Steve Kim to perform quartz crystal microbalance experiments and spectral microscopy experiments; Some of these results were published in a 2015 *Langmuir* paper.

*Presentations:*

- Rosi Invited Seminar, Northwestern University (2011)
- Rosi Invited Seminar, University of Illinois (2011)
- Rosi Department Seminar, University of Pittsburgh (2011)
- Rosi Invited Seminar, St. Francis University (2011)
- Rosi Invited Seminar, Science 2011, University of Pittsburgh (2011)
- Rosi Invited Seminar, Chatham University (2012)
- Rosi Invited Seminar, Spring National ACS Meeting (2012)
- Rosi Invited Seminar, Spring National MRS Meeting (2012)
- Chengyi Song Poster Presentation, Spring National ACS Meeting (2012)

- Leekyoung Hwang Poster Presentation, Spring National ACS Meeting (2012)
- Kavli Frontiers of Science Symposium (2012)
- Rosi Invited Seminar, Fall National ACS Meeting (2012)
- Rosi poster presentation, Argonne National Laboratory (2013)
- Rosi Invited Seminar, University of South Florida (2013)
- Chen Zhang poster presentation, ACS Central Regional Meeting (2013)
- Chen Zhang poster presentation, Science 2013, University of Pittsburgh (2013)
- Chen Zhang, poster presentation, ACS Spring National Meeting (2014)
- Rosi Invited Seminar, Brandeis University (2014)
- Andre Merg, poster presentation, Innovations in Materials Chemistry, U.Pitt (2014)
- Chen Zhang, poster presentation, Innovations in Materials Chemistry, U.Pitt (2014)
- Andre Merg, poster presentation, Noble Metal Nanoparticles GRC (2014)
- Chen Zhang, poster presentation, Fall National ACS Meeting (2014)
- Rosi Invited Seminar, Fall National ACS Meeting (2014)
- Rosi Invited Seminar, University of California, Berkeley (2014)
- Rosi Invited Seminar, ACS Central Regional Meeting (2014)
- Chen Zhang, poster presentation, ACS Central Regional Meeting (2014)
- Rosi Invited Seminar, Boston University (2014)
- Rosi Invited Seminar, Fall National MRS Meeting (2014)
- Rosi Invited Seminar, University of Dallas (2015)
- Rosi Invited Keynote Lecture, IUPAC Meeting (2015)
- Rosi Invited Seminar, UNIST, South Korea (2015)
- Rosi Invited Seminar, Youngstown State University (2015)
- Andre Merg, poster presentation, Pacifichem (2015)
- Andre Merg, oral presentation, Innovations in Materials Chemistry, U.Pitt (2016)
- Andre Merg, oral presentation, ACS Central Regional Meeting (2016)
- Yicheng Zhou, poster presentation, ACS Central Regional Meeting (2016)
- Andre Merg, oral presentation, Fall National ACS Meeting (2016)